The history of corrosion technology (up to about the time of the First World War)

Thesis

THE HISTORY OF CORROSION TECHNOLOGY

(up to about the time of the First World War)

BY

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C O N T E N T S

9. TINPLATING

ABSTRACT

In this work, the author examines the problems that metallic corrosion has caused through the ages, and the attempts that have been made to combat it, particularly from the technological point of view.

The period under special consideration is the nineteenth century. During that time, two aspects of the industrial revolution highlighted the problems that corrosion can cause.

The quantity of iron and steel produced, increased enormously, so an ever increasing volume of metal became exposed to air and water. At the same time, the environmental pollution from the very furnaces and other manufacturing establishments that were producing the iron and steel, served to increase the aggressive nature of the corrosive attack.

These two factors combined to make industrialists fully aware of the magnitude of the problem and this resulted in detailed investigations being carried out to attempt to quantify the amount of corrosion occuring in various environments and with different grades of iron and steel. During the nineteenth century, engineers tended to concentrate on ferrous metals and scientists on non-ferrous metals.

Centuries ago, it was appreciated that the important factor in the prevention of corrosion, was for the metal to be separated from any aggressive environment. Many attempts have been made since then to find a covering that would become firmly attached to the metal surface and prevent ingress of the corroding media.

Until about 1836, these attempts had been made empirically, but at that time, the principles of galvanic protection, which had been established earlier in the century, began to be put into practice.

Tin had been applied as a covering for centuries, prior to these discoveries, primarily because of its decorative appeal. Scientists were now able to appreciate that the protection given by tin was just mechanical, whereas zinc, bestowed both mechanical and electrochemical protection. This realisation increased the popularity of zinc as a protective material.

Electroplating became firmly established during the century, especially when 'magneto-electric machines' superceded the battery and provided a reliable current supply. Little scientific thought was given to painting until nearly the end of the century, when red lead became firmly established as the most suitable base for use.

CHAPTER 1

INTRODUCTION

Metallic corrosion is a phenomenon that is nearly as old as technology itself, since it involves the interaction of metals with their environment and because metals have been used in technology since the bronze age.

Until relatively recently, the word 'rust' or 'rusting' tended to be in more popular usage than 'corrosion' since it describes the specialised form of corrosion relevant to iron and steel. The word 'rust' appears to have a much earlier origin than 'corrosion' since it is derived from a Pre-Teutonic language.(1) This is an earlier stage of the prehistoric language from which the Germanic languages developed. The original word in this language was 'rudhusto', the letters 'rud' being in relation to the colour red.

Rust can be described as a red or orange covering upon the surface of iron or steel formed by oxidation, especially through the action of air and/or moisture.

A passing mention of 'rusting' has been made on occasions in prose and verse(2 - 7) often in the context of rusting swords. Possibly the first recorded mention in verse of the word corrosion or its cognate 'corosif' was by Chaucer in 1386 when he referred to:-(8)

"waters corosif"

The original meaning of the word to 'corrode' was to:-(9)

"eat into or gnaw away"

and gradually by the Middle English period the definition was extended to mean:-

"to wear away or destroy as if by eating or gnawing away the texture."(9)

Fig. 1. represents possibly the earliest copy of a definition of the word 'corrosion'(10) (The definition given however, we now know to be incorrect, since the action of corrosion is one of oxidation and not reduction).

Contuſion is the beating of groſſe bodies into ſmaller or very ſubtill part.

Corroſion is calcination, reducing things coagulated, by the corroding ſpirits of ſalt, ſulphur, by wine-vineger diſtilled, *Aqua fortis*, &c. into calx.

Cribration is the preparation of medicaments by a ſiue, or ſearce.

(10)

FIG. 1 POSSIBLY THE EARLIEST COPY OF A DEFINITION OF 'CORROSION'.
(THIS WAS IN A MEDICAL CONTEXT.)

By 1760, a more technical meaning was given by Keysler:-(2.)

"Green borax or chrysocolla is nothing else but copper turned into rust by corrosion."

Today we are aware that the action of metallic corrosion is very complex and varies considerably from system to system. Consequently, any definition must be very broad to cover all eventualities and one way of defining it would be to state it as:-

> A complex process involving a chemical or electrochemical reaction between a metal and its environment, usually resulting in a deterioration in the properties and/or appearance of the metal. Slight variations in the composition of a metal or its environment can greatly effect the corrosion rate of a metal and the manner of the corrosion.

In this work, we examine in the wider context, the effect that corrosion has had on society; how science and technology reacted to this problem and how corrosion has influenced technological development.

CHAPTER 2

HISTORICAL BACKGROUND

2.1. CORROSION IN ANTIQUITY

So far we have considered the use of the words corrosion, rust and their early appearances in verse and prose.

It is now intended to consider some of the problems that have been caused by corrosion through the ages and methods that have been tried for protection. This is a background chapter to highlight important events, many points of which will be elaborated later.

Reference to corrosion and corrosion protection were made during Roman times by Pliny in the chapters of his work dealing with 'chemical subjects'.(11)

Caius Plinius Secundus, was born, according to an unknown biographer, in A.D. 23 and perished in the eruption of Vesuvius in 79 A.D.

He appears to have been a man of many interests and was a friend and associate of the Emperor Vespasian.

Amongst his observations was that:-

"When bronzes are cleaned, they rust more quickly than when left alone, unless rubbed over with oil. Tar is said to protect them most perfectly. For many years, bronze has been used for lasting memorials in general.

"The sculptor Aristonidas, wishing to depict the rage of Athamas giving repentance, after he had hurled his son Learchus to his death, alloyed iron with copper, so that the blush of shame might be brought out by the rust of the iron glowing through the shining surface of the bronze. This statue stands in Rhodes unto this day."

Rust was endowed with such a wide variety of remarkable properties and it is particularly surprising that it should have been considered to have medicinal properties.(12)

Pliny tells how Alexander the Great, during his wars against the Persians, had built an iron bridge over the Euphrates at Zeugma.

The original iron chains lasted well, but chains which had been replaced at a later date, during the early middle ages, were rusting while the old chains remained in good condition.

It could well have been that both the technique and basic iron ore used at the two periods were different. Alexander, during his travels, visited India and craftsmen in his party may have observed methods of iron manufacture able to produce material that had the property of forming natural protective films on its surface. The Romans never mastered this technique.

There is some prima facie evidence that the resistance of iron to corrosion did deteriorate when primitive methods of manufacture gave way to large scale metallurgical processes. Pillars and other objects of iron erected in the East many centuries ago are still free from rust. The best known example is the Delhi Pillar which was erected some considerable time after Alexander's excursions there, in the fourth century A.D. This remains in the twentieth century, unrusted, although the appearance suggests the formation of a natural protective film and illustrates the advanced state of Indian technology at that time.

The Iron Pillar at Delhi, was constructed from forge - welded wrought iron about 1600 years ago.(12) It is 720 cm. high, of which 50 cm. is below ground level and 45 cm. above ground is surrounded by a stone platform. The part of the pillar which is below ground has been observed to be covered by a rust layer about 1 cm. thick, and shows deep pitting. Above ground, the pillar is coated by a protective oxide film 50 - 500 μm. thick.

The technique of manufacture is particularly interesting. In contrast to modern steel, it has never been molten. In ancient times, wrought iron was manufactured from iron ore, in this case it is considered to have been weathered magnetite obtained by surface quarrying. The ore was bedded intermittently with charcoal in a charcoal-fired small furnace with a foot driven wide bellow. The lumps of iron 'sponge' so

obtained were then hammer-forged in order to squeeze out most of the slag. At the same time, most of the carbon still present in the iron was oxidized. Even before the beginning of our chronology, the old Hindus are said to have mastered the art of melting wrought iron in small crucibles to form steel, from which they prepared surgical instruments and stone-cutting tools.(13) This process appears to have been carried out only on a small scale.

It is probable that in these early periods of civilization, the corrosion of metallic implements and structures was by far a less serious factor in restricting their life than mechanical wear and tear.

The strength we now associate with iron and steel only became a reality in the nineteenth century when alloying elements and heat treatment were introduced. There were also other factors, which will be discussed later.

2.2. INFLUENCE OF INDUSTRIAL DEVELOPMENT

In recent centuries, the increasing use of coal as a fuel has filled the atmosphere in industrial and highly populated districts with sulphur dioxide and the rate of corrosion in these areas in the same situations would certainly undergo rapid increase, possibly the influence of smelting being a contributory factor.

When coal replaced wood as a fuel for heating, and coke replaced charcoal as a reducing agent for smelting ores, the atmosphere in industrial areas became polluted with sulphurous oxides, whilst the iron or steel produced came to contain phosphorus and sulphur. Either sulphur dioxide in the air or sulphur in the metal increases the probability that corrosion will start when a small area of metal is exposed to moist air, and often increases the rapidity with which that corrosion will proceed.

Such damage must have been appreciable before the end of the eighteenth century but it was only in the nineteenth century that efforts were made to examine the basic causes of corrosion.

In Great Britain, cases are known of cast iron bridges which remained relatively unattacked for well over a century. Fig. 2 illustrates such a bridge which existed until the early twentieth century, at Merthyr. A contributory factor to this long life could be the presence of a protective oxide film formed when the bridge was erected prior to the onset of atmospheric pollution.

The first major cast iron bridge was constructed in Shropshire in 1779 and from this period until the end of the eighteenth century, there was a gradual increase in the use of cast iron for constructional purposes.

During the early decades of the nineteenth century however, there was a vast increase in this demand and consequently, it became more necessary for scientists and engineers to gain an understanding of the practical consequences of corrosion.

Investigations of a limited nature were carried out in France by Guibourt[14] in 1818 and by Chevallier in Germany in 1828[15] but they were of little practical value. Consequently the British Association decided to grant a sum of money to undertake an extensive series of experiments to investigate the chemical and mechanical effects and changes produced on cast and wrought iron by the continued action of sea water at various temperatures. These very comprehensive series of investigations were reported by Mallet in 1838,[16] 1840,[17] and 1843[18] and comprised 198 pages. Unfortunately there is little biographical detail of Mallet's personal life available.

They were to be the first of many carried out during the nineteenth century, which in part contrasted the merits of iron and steel. Great differences of opinion were to be expressed on this topic and various experimenters obtained results which were apparently most contradictory. These differences arose probably on account of conclusions being drawn from limited observation, or special circumstances. Much confusion arose from failing to recognise that the conditions in fresh water, salt water, the interiors of boilers or in diluted acids were all different and that a specimen which may very successfully resist corrosion in one of these cases may readily oxidise in another.

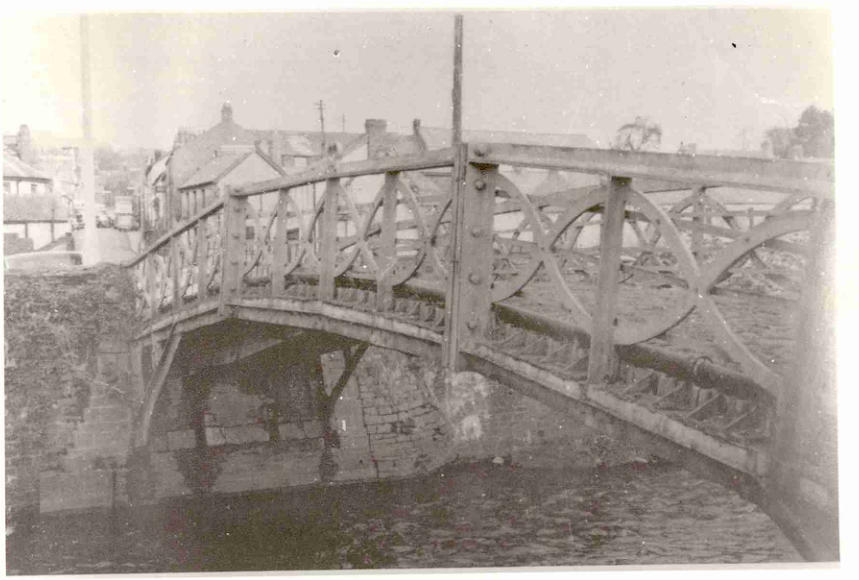


FIG. 2. A CAST IRON BRIDGE THAT WAS AT MERTHYR, SOUTH WALES, UNTIL THE EARLY TWENTIETH CENTURY

(Ack. Nat. Mus. Wales)

In many cases, the experimenter would provide such little detail of the conditions under which the results were obtained that an analysis would be impossible.

Around the mid-nineteenth century, interest was mainly centred around the relative merits of the corrosion-resisting properties of wrought iron and steel. The quantity of iron and steel manufactured however, was small, and was produced by a large number of small firms.

Later in the century, several large manufacturers of steel had emerged producing material in large quantities, but the confused situation in corrosion testing techniques still existed and this was fully exploited by these industrialists who had large sums of money at stake.

At this time the materials under comparison were steel and cast iron.

Manufacturers of steel such as Bessemer and Siemens would state results by scientists in their employment, illustrating how superior the corrosion-resisting properties of steel were in comparison with those of cast iron. Advocates of cast iron would do likewise. Pitched verbal battles were enacted between the various contenders at meetings, usually arranged by the Iron and Steel Institute.[19] Eventually, the battle for increased steel usage was not won on account of any superior corrosion-resisting properties steel had, but because of its increased strength in tension. Reports appear in the literature of cases of specific interest. These were namely railway bridges, office blocks and steam boilers.

In railway tunnels and bridges, problems of corrosion appeared to be connected with the ingress of steam and sulphur laden smoke through the riveted joints.[20] [21] [22] Following the riveting operation the metal around the rivets would be in a highly stressed state and in contact with this corrosive medium rapid failure would often occur due to stress-corrosion.

During this period of technological advance, there was no comparative systematic development of any paint systems to protect the ever larger

structures that were being built. The first scientific testing of any paint system occured in the last decade of the nineteenth century, establishing the superiority of red lead.

Another major problem was the occasional corrosion of steel used in office block construction which was encased in cement and brickwork. Some builders presumed that full protection was afforded irrespective of the composition of the cement.(23) (24)

The effect of corrosion on steam boilers was more dramatic than on other engineering components. This was because failure was very closely linked with a loss of life when boilers exploded. Because of this aspect, both insurance companies and Parliament became more deeply involved in these instances of corrosion than in any other. Consequently, nearly all the early information on the effect of corrosion in its various forms has to be gleaned from the reports of insurance inspectors and government officials. The inspectors were, in general, very experienced engineers and were the only people both to investigate the corrosion in boilers and to produce reports for their companies and professional journals.

The development of an understanding of corrosion in boilers is consequently very closely linked with the development of the boiler insurance Companies and the gradual enlightenment of successive governments.

However, it is necessary to emphasise that the percentage of explosions attributed to corrosion was usually less than 50 per-cent.(25) Many failures especially during the mid-nineteenth century, were due to poor design, unsatisfactory materials and bad boiler management. In 1862 only 14 per-cent of accidents were due to corrosion,(26) but as the principles of boiler design began to be appreciated, problems associated with corrosion began to take a larger share of explosions that occured.

In very broad terms engineers took a far greater interest in ferrous rather than in non-ferrous metals, in the nineteenth century. This was primarily because of the superior mechanical properties that ferrous metals possessed.

Scientists however, had a far broader interest but tended to concentrate on the range of non-ferrous metals.

The science of corrosion had its first period of rapid advancement in the first half of the nineteenth century. The details of the theories relating to this development are given later(chapter 8) This advancement was a result of intense and sustained scientific interest and activity aroused by the invention of the voltaic pile[26] and the controversy over the nature and source of galvanic current.

A non-ferrous metal that has played an important role in mans development from the time of antiquity is lead.

Long before the principles of galvanic corrosion[27] were understood a report was mentioned by Bryant of how in 1681, the Navy Board decided to remove lead sheathing from ships to prevent the rusting of rudder irons and bolt heads. While this event was in progress, Pepys took King Charles II, who was an expert on shipbuilding, to investigate the problem. The King could not suggest a reason for this corrosion "unless the lead has something corrosive in it."

This was over 150 years before Mushet investigated the impurities in copper as a source of corrosion.[28]

Throughout history, lead has been used mainly for the construction of water pipes and cisterns, although the material has had a wide variety of applications. The action of water upon lead varies considerably between localities and as early as 1834[29] the 'character of the water' as indicated by hardness or softness was considered important. Investigations into this action tended to take place in localities where the water attacked the piping and many extensive tests were carried out.[30]

Of the non-ferrous metals, copper and zinc were of considerable interest to scientists and engineers in the nineteenth century, primarily because of their connections with developments from the galvanic battery. This will be dealt with in detail later. Zinc was closely linked with copper as a sacrificial partner and because of this relationship, an increased use was found for the metal.

It was only during the last decade of the nineteenth century, that there was sufficient aluminium available for it to be used in quantity. When alloyed with certain other metals it was sufficiently strong to be used as an architectural material.(31) A main reason for its popularity was its lightness. It was also found that any minute quantities entering the solution did not cause poisoning.(32)

2.3. ATTEMPTS TO COMBAT CORROSION

2.3.1. Alloying Elements

The influence of chemical composition upon the corrosibility of iron was studied at various times during the nineteenth century, but usually only in the context of a much wider investigation into the effect of composition on other properties. Usually the investigator was interested in factors which would improve the mechanical properties of the material. However, just occasionally, a mention would be made of any observations of corrosion or corrosion resisting properties that an alloy would have.

From the investigations of Stodart and Faraday(33 to 38) around 1820, research workers tried to keep pace with the rapid rise in technology. The developments of the lathe and other machinery demanded cutting tools of progressively greater strength and toughness as the speeds of operation increased. Faraday was generally regarded as a most observant man apart from his many sided scientific genius. It was upon these casual observations and impressions that we rely to give some insight into opinions held at that time regarding the relative resistance that alloys with iron bestowed. Unfortunately, few other workers at that time wavered from the task before them, or if they did, none of their observations on corrosion resisting properties found their way into the papers they wrote.

Faraday in fact, did a few corrosion tests on alloys, but we are indebted to the extensive corrosion testing that was carried out by Mallet around 1840 for the first insight into the influence of alloying materials. Even Mallet's contribution to alloying effects was very small

when compared with the three extensive papers he gave in the years 1836[16] 1840[17] and 1843.[18]

For a period of about 50 years, virtually no testing of the effect of alloying additions on corrosion resisting properties was carried out, although many papers were given on the influence of these additions on the strength of the material. In the last decade of the century, reports of Hadfield[39] contained small sections on corrosion testing and from these reports it is possible to compile and illustrate the properties of the alloys as known at that time.

2.3.2. Magnetic Oxides

A number of processes were developed in the nineteenth century for producing a black or magnetic oxide coating on the parent metal to give protection against corrosion.

The French chemist Lavoisier[40] mentioned that he observed the presence of the oxide in 1781, but Barff[41] in 1887 was the first to investigate in any detail the protective properties of the coating with a view to commercial development.

From the publications of Barff,[41,42,43] G. Bower an industrialist from St. Neots in Huntingdonshire, first learned about the process and endeavoured to dispense with steam, which had been the basis of Barff's work, and use air.[44 to 48] At first, he was unsuccessful in obtaining the desired result, since the duration of the treatment necessary to produce a good coating of magnetic oxide also resulted in the formation of the red or ferric oxide. To overcome this difficulty, he made use of producer gas to reduce the ferric oxide. Later his son, A. Bower, acquired the patent and established the Bower-Barff process,[49,50,51] details of which are given later.

The use of this coat was restricted for several reasons, which included the limitation in the physical sizes of components that could be treated. Another problem was that the magnetic oxide film was too brittle to

withstand deformation and would crack and flake off. The process was also a costly one.

Magnetic oxide is strongly electro-negative to iron, and like similar coats, it ceases to fulfil its proper function as soon as its continuity is broken. Once the iron underneath was exposed, it then commenced to function as an accelerator of the corrosion of the electro-positive iron, because of the high corrosion current density at these points.

From the outset, these difficulties were stressed by the minority of the commentators,[32] the rest giving unqualified praise for the process.[53,54] The reasons for this unqualified admiration from many of the observers was that unsuitable field tests had been carried out, testing the coating under conditions in which it would rarely be used. The voices of dissent came from more practical men and they were later proved to be correct.

Nevertheless, for some time companies successfully operated using the process to coat materials, but the scope of application was far less then had originally been envisaged. Plants were also built on the Continent and in America[55] and within the confines of these stated limitations, provided a useful service well into the twentieth century.

2.3.3. Paints, Enamels and Chalk

Although the Romans had methods of protection against corrosion, using white lead, it was not until an anonymous paper appeared in Dingl. J.[56] in 1822 that there were indications of any serious attempts to protect against corrosion in the nineteenth century using paints or varnishes.

The first comprehensive series of tests on various paints and varnishes was carried out between 1838[16] and 1840[17] by Mallet at the instigation of the British Association. These tests, however, formed only a very small part of a major investigation into the problems of corrosion and went practically unnoticed.

Mallet was not internationally famous like such a personage as Faraday. His work in England went virtually unrecorded in Europe, consequently no other scientists at that time either in Europe or even in England were stimulated into continuing investigations into varnish or paint systems on a scientific basis on the pattern that Mallet had established.

For a period of some 50 years, the 'dark ages' descended in which many diverse compositions were introduced, most of which produced disastrous results. Virtually no scientific tests or developments were recorded. Compositions were patented, the constituents of which may well in many cases have been inert towards iron, but when mixed together, were useless.

By the last decade of the century, it had become customary to make rational judgements in most fields of scientific endeavour on the basis of practical experiments. These ideas had spread even into the fields of paint and varnish application. During that decade comprehensive tests were carried out and red lead, which by then had widespread use, was found to be by far the best protective paint pigment to use to combat corrosion in an atmospheric environment.(57) SEE also Ref (58)

An early record of the use of tar as a protection against corrosion is given in Dingl: J. in 1826.(59) This material and other products distilled from coal and wood continued to be frequently used for this purpose throughout the nineteenth century.

The first record of clay and chalk being used specifically to prevent corrosion, was in 1814(60) and interest in these materials in the nineteenth century appears to have been confined to the Continent for civil engineering application in connection with pipe networks.

Enamel was first discussed in detail in 1842 by Mallet(61) and introduced in quantity into Britain from France in 1850.(62) It was applied to corrugated iron sheets for roofing as a protective material,

but there is little evidence that this application for enamel was pursued, the reason for this probably being the direct competition it received from lower priced galvanized material.

No scientific reasoning appears to have been displayed in the choice of any of these coatings. The main criterion appears to have been in providing a thick, sometimes viscous coating, the consideration being that thickness was somehow proportional to impregnability.

2.3.4. Metallic Coats

Of the metals used as protective coatings, tin stands foremost in its length of service to mankind. By the year 1800, a tinplate industry, small in scale and subsidiary to the iron industry had become securely established in Great Britain.(63) The commercial smelting of zinc only became a viable proposition in the mid eighteenth century and this consequently held up the commencement of the zinc coating process.

In early historical times, all metals were valuable and the ability of tin to spread thinly and evenly on the surface of other metals made it possible to achieve the full decorative effect of tin without using much material. At the present time, it is customary to regard tin for its protective effect on other metals rather than for decorative appeal.

An early description on the tinning of iron was given in the twelfth century by the work of Theophilus Rugerus:-(64)

"Whatever you wish to tin over in iron, file first before you touch it with the hand, put it in the pot of melted tin with grease and stir with tongs till it becomes white."

The idea of tinning hammered iron sheet, so forming a durable material from which objects could afterwards be fashioned, was a natural result of the recognition that a tin coating transformed iron into a more lasting material. When this happened, is not precisely known. It would appear however, that Bavaria(63) was the original home of the industry in the early fourteenth century.

The industry spread to Saxony, where a tinplate works was set up in 1536 and to Bohemia where a successful plant was started in 1570. The Saxon industry prospered so that by 1618 there were more than twelve tinplate works in Saxony and there was a good export business to many countries, including England. There followed, however, a period of disruption of the industry, owing to the outbreak of the Thirty Years' War.(63) The production difficulties brought about by the war, together with the fact that Cornish tin had been exported to Germany since 1575, probably brought about interest in the development of a tinplate industry in England.

John Tilte saw the possibilities of developments in England in 1623 but probably through lack of capital, little was completed. It was however, Andrew Yarranton who took the first practical steps to establish the tinplate industry in 1665. In that year he visited Saxony and was able to get an excellent insight into the practical working of the industry.(65)

On his return to Britain, Yarranton produced some tinplate, but he did not succeed in establishing an industry.

He described his ultimate failure as being due to the opposition of influential people who prevented patents being granted.

Although the manufacturing industry was unable to gain establishment in Britain at this time, there must have been considerable business in imported plate, since in 1670 a charter of Incorporation was granted to the Worshipful Company of Tin-Plate Workers.(66)

The next event of significance occurred about 1720, when Capel and John Hanbury became the first to establish a viable plant, at Pontypool in South Wales.(67)

When success finally came, it was due to the technical advantage resulting from the adaption of the rolling mill to make iron sheet for tinning. The introduction of rolled iron sheet instead of the earlier hammered material was a technical development of great importance.

At first, tin-plate manufacture expanded slowly in Great Britain and only a few attempts were made to follow the Pontypool example. Growth was slow for two probable reasons. Firstly, knowledge of technical processes spread slowly and the training of skilled workers was a lengthy business. Secondly, the market for tin-plate ware suffered from competition of japanned and lacquered articles which were largely imported.

The gradual growth in the British industry was largely to cater for the demand in the home market created by the drying up of the German source due to the Thirty Years War. When the war ended in 1618, imports of German tin-plate did not recover, only small quantities being imported after that date.

From the mid-century the tin-plate industry expanded more rapidly. The adoption of the rolling process for making sheets not only gave British tin-plate a finer gloss but also enabled British makers to manufacture tin-plate more cheaply than the German producers. They were slow to adopt this process for the manufacture of tin-plate.

Improvements were also made in the pickling and tinning process(63) and as a result, German tin-plate was prised out of the British market. In the home market, conditions had improved with the growth in demand for japanned and tinned ware produced in the Midlands.

Although tin-plate works were built in different parts of Britain, they were mainly situated in the West of the Country, in the West Midlands, the Forest of Dean, and South Wales. Cornwall unfortunately had none of the requirements for a thriving tin-plate industry; i.e. major iron producing manufacturers, sufficient wood for fuel or water in a suitable location to provide hydraulic power, although some tin mines were situated there. The geographical remoteness of the area from potential customers would also have been a decisive disadvantage.

Works were set up at places like Kidwelly, Melingriffith, Caerleon and Redbrook where water for power and transport was available. The

tinplate manufacture grew more rapidly in South Wales in the late eighteenth century than in the Midlands or elsewhere. This was probably because the alternative and probably more profitable uses for iron in the Midlands absorbed the attentions of the ironmasters there, whereas the forgemasters in South Wales, lacking such outlets found it more advantageous to concentrate on tinplate making which yielded a greater return than bar iron production.

Up to about 1835, developments in tinplating had been by practical innovation[68] rather than by scientific reasoning and no successful attempt had been made to explain in any precise way the fundamentals of the coating; especially the behaviour of the coating when in contact with other metals. By 1835, scientists were able to appreciate the principles of the electrochemical series and to realise that although tin had not the protective power of zinc, yet pinhole corrosion which is liable to occur, does not occur very often.[69,70] They appreciated that tinplate represents a different corrosion situation with tin being cathodic to iron under normal conditions. Although tin cans had been produced for over 10 years by that time, the state of the science was not advanced enough to appreciate that organic acids present in foodstuff form complexes with the tin, resulting in a lowered activity of the stannous ions with the tin inside the can becoming anodic with respect to the iron in that specific environment.

During the second half of the nineteenth century, production techniques continued to improve[71] and the Welsh tinplating industry reigned supreme until the introduction of the McKinley tarriff in 1890 lost the American market and caused a great slump in the Welsh Industry.[72] The resilient Welsh however, gradually built up the home market and found new outlets in the developing countries.

During the nineteenth century, a process which became known as galvanizing developed and replaced tinplating in many of its traditional roles. The process involved the use of molten zinc and utilised the fact

that zinc provided a sacrificial covering to protect iron and steel.

The word 'galvanizing' was derived from the name of an Italian physiologist, L. Galvani who in 1786 made the observation that when the bodies of dead frogs were hung on an iron frame by copper wires, twitching of the legs occured whenever they touched the iron.

The word "galvanizing" was first introduced by M. Sorel of Paris in a patent of July 1837.(73)

"_ _ _ means of preserving iron ffom rust by galvanism" and

"This addition has for its object some practical and very important details on the art of galvanizing iron."

Sorel's use of terminology to describe his work was in some ways unfortunate since the principles behind his developments would have been better attributed to the work of another Italian Professor Volta.(74) He showed that the electrical phenomenon was not as Galvani had believed, of animal origin, but resulted from the contact of two dissimilar metals.

The word galvanizing did not in fact refer to the process of coating but to the fundumental property offered by this coating. It concerned the protection given by the 'galvanic effect' which was the term used by Sorel to describe the principle of one of his earlier patents filed in 1837.(73)

Although the origin of the word related to the coating, it became more and more confused with the process used for applying the coating, i.e. dipping in molten zinc.

At the beginningof the nineteenth century, galvanizing, unlike tin-plating, was in its infancy.

The main reason for this delay in development was that zinc had only been commercially smelted for the first time in the mid-eighteenth century.

Malouin(SEE 74) had discovered galvanizing, but an early application had been as a cheap substitute for tinplate and with "poisonous juices" being produced,the coating suffered unpopularity. Since it was inexpensive, it began to be used for protecting metal from corrosion.

Up to 1837, developments in hot dip galvanizing had been made by empiricism rather than by scientific understanding. Malouin (SEE 74) had earlier discovered hot galvanizing but could not in any precise way explain the fundamentals of the coating.

By 1837, the great research of Volta[75] and Davy[76,77,78] had taken place and scientists were able to give expression to Sorel's[73] work of that year. Originally, galvanizing had been used with small articles then gradually extended to semi-fabricated products. Up to 1846 there appears to have been little interaction in the development of tinplating and galvanizing processes. There could be several reasons for this:- tinplating developed in reasonably isolated Welsh communities but galvanizing plants were situated in industrial areas mainly in the Midlands.

In 1846 sheet galvanizing as a separate industry developed[79] and after considerable modification, a galvanizing machine was made, based on one used in tinplating. The first rolling and galvanizing plant was situated at Wolverhampton.

With this development in the technology, the speed of galvanizing increased and the sheets were in contact with the spelter for a much shorter time. At this stage, the technology had once again outpaced men's knowledge.

The hand process had been sufficiently slow for the sheet to reach an equalising temperature with the spelter, resulting in a firm bond between the materials.

Interest in wire galvanizing[80] started about 1850 with the formation of the telegraph companies and the development of the industry came from a patent by Bedson in 1860.[80]

Galvanizing companies were involved in a government enquiry[81] investigating the poor working conditions of the men and also litigation with councils over waste pickle disposal, nevertheless, one company which was formed in 1838 is still thriving today.[82]

The electroplating industry can be considered to have started in 1840, when the successful working of certain solutions was made known to Messrs. Elkington and Co. of Birmingham by a surgeon, Dr. John Wright.(83)

From the beginning of the century, a knowledge that metals could be electrodeposited had been appreciated,(84) but up to 1836 developments that had taken place had been by empiricism rather than by scientific understanding.

A glimmer of understanding had been expressed by De la Rue (85) in 1834 which probably resulted in the near simultaneous publications in 1839 by Jacobi(86) of Russia, Jordon(87) of London and Spencer(88) of Liverpool on electrotyping copper.

In 1840, Messrs. G.R. and H. Elkington coated ornaments with silver and gold by immersing them in solutions of these metals.(89) Wright however, discovered that by the use of potassium cyanide, thick deposits of silver and gold could be obtained, and he sold his discovery to the Elkingtons.(83) Their workers then developed the process further.

In depositing silver, adhesion between the underlying metal and silver was unreliable, but the difficulty for deposition on copper was overcome by Leeson(90) who first covered the metal with a thin mercury film and consequently obtained perfect adhesion.

Iron and steel have no adhesive attraction for mercury, but by first electrodepositing in an alkali bath, a thin coating of copper on the iron, ie 'quicking', this was achieved.

In 1847, W. Milwood, a 'practical' plater, produced a bright silver plate by adding carbon disulphide to the plating vat.(91)

In 1863, the dynamo made its appearance as a substitute for batteries. As early as 1842, Woolrich had invented his novel 'Magneto-Electric' Machine, but the first satisfactory dynamo was the Gramme machine produced in 1871. Batteries were satisfactory if only small currents were required as in the electrodeposition of silver and gold. By this time however, Adams(94) had developed the practical process of electrodeposition of nickel in America, and for this, a much larger current was necessary. This was provided by the dynamo. By the construction of suitable dynamo machines, a great

impetus was given to the electroplating industry. They supplemented the ordinary cell apparatus and founded the basis for modern electroplating.

The role of a coating as a means of protection against corrosion, is essentially to insulate the metal from the external medium so preventing the formation of microcells on the metal surface. The choice of the type of coating depends on the conditions under which the metal is to be used, and the protective properties will depend on the quality of the prior preparation of the surface.

The noble metals which were the first to be successfully electrodeposited in 1840, were used primarily for aesthetic reasons.[95] Silver, gold and also copper are less electropositive than iron, zinc and their alloys in the electrochemical series and therefore protection against corrosion is possible only if pores and bare parts are absent in the coating. Chromium is more electronegative than iron but owing to the strong tendency of chromium to become passive even in air, mechanical protection only is given.

The sherardizing process was discovered by chance by the English inventor Sherard Cowper-Coles in 1900. When iron or steel is heated to certain temperatures in zinc dust an amalgamation of the two metals occurs with the formation of a protective iron - zinc alloy. The principles involved in sherardizing were not entirely unknown previous to this. In 1838 Berry[96] took out a patent in which he coated iron and copper in a similar manner and in 1896 Roberts-Austin[97] alloyed gold and lead at temperatures well below the melting point of lead.

However, it was Cowper-Coles[98] who eventually developed a workable technique. He produced a zinc coating on iron and steel unintentionally during the annealing of some samples. Powdered zinc was being used as a supposedly inert substance for packing, in order to exclude air. Subsequent examination showed that the zinc had not only coated the iron, but had alloyed with it and penetrated the iron surface. In these events, Cowper-

Coles showed two of the criteria required for scientific genius; these being to be keenly observant of events during experimentation and to be able to interpret them.

Cowper-Coles and later Trood,[99] developed the process producing zinc coatings on small objects with longer life than many galvanized coats.

CHAPTER 3

IMPORTANT INVESTIGATIONS

3.1. PHYSICAL CHANGES IN METALS

3.1.1. Mallets major contribution

The first comprehensive series of investigations into the corrosion of iron and steel were carried out by Mallet and reported in three reports in 1838[16] 1840[17] and 1843.[18]

In the first series of experiments, cast iron was exposed for 387 days in clear sea water at 46 - 58°F. and at 110 - 125°F. in polluted sea water, in fresh clear river and in polluted tidal river water. In the second series of experiments, the same materials were exposed for an additional 732 days and the wrought irons and steels were tested concurrently under five different conditions of exposure. In addition, the cast irons were exposed to the atmosphere of Dublin for 539 days.

For these experiments, Mallet melted the cast iron in crucibles to avoid contamination and cast as nearly as possible, into sections five inches by one inch thick, and five inches by a quarter of an inch thick, respectively, and cooled at the same rate; the encased specimens were then sunk into the water, the form of the boxes allowing free access to the water.

The results showed that under conditions of clear sea water, the greatest amount of corrosion was produced and that foul sea water was almost as destructive. The least corrosion was produced by clear river water. Other specimens were exposed to the air.

His investigations led him to believe that the great elements of difference in corrosion as regards iron itself are:- (1). The degree of homogeneity of substance of the metal and especially of its surface. (2). The degree of density of the metal and state of its crystalline arrangement (3). The amount of uncombined carbon or suspended graphite contained in the iron.

For practical purposes, Mallet deduced that from three to four-tenths of an inch in depth of cast iron, one inch thick, and about six-tenths of an inch in depth of wrought iron will be destroyed in a century in clear sea water. The accuracy of these deductions was closely verified by comparison with the effect produced by clear sea water upon the guns taken from the wreck of H.M.S. 'Edgar', which after immersion for one hundred and twenty nine years, were corroded to a depth of $\frac{7}{8}$ of an inch; and also by comparison with iron from the 'Royal George,' immersed for forty-eight years, with a corrosion of from one half to three-fourths of an inch in depth.

3.1.2. Observations of weight and volume changes

T. Stevenson gives examples of more rapid decay than those found by Mallet. In his work published in 1859, he states that on completion of the Bell Rock lighthouse, R. Stevenson directed that cast iron tramways consisting of rails with open gratings between, and supported on standards, to be fixed to the rock and that:-(100)

"Many of these gratings which are not constantly immersed are now decayed in different places, cavities having been formed on their upper surfaces fully half an inch deep, thus giving one inch to the century for castings an inch square," and again, one of the bars which was quite free from air holes presented no external appearance of decay but had its specific gravity reduced to 5.63 and its transverse strength from 4068lbs. to 2352lbs. having lost nearly half its strength in about fifty years."(100)

Further work was carried out by Adie(101) in 1845, he showed by quantitative experiments that iron was more vigorously attacked by sea water in the presence of air, than by fresh water under similar conditions. He found, for example, that twenty pieces of wrought iron wire immersed in sea water for eighty days lost 2.6 grains in weight, whereas in fresh water the loss amounted to only three quarters of this. His experiments followed very closely on those of Mallet and appear to duplicate in essence much of his work. He did however, show that oxygen was less

soluble in sea water than in fresh water and later investigations subsequently confirmed this. That iron is attacked by sea water even in the complete absence of air appears to have been first showed by Payen,[102] He did however find that iron may be kept for an indefinite time in fresh water which has been freed from dissolved air through boiling.

An annonymous contributer to Engineering[103] mentioned an experiment in which cast iron cubes with one cm. sides were placed in a bottle containing 80 cubic centimeters of very dilute acid and the bottle corked. Amongst the acids tried were sulphuric, hydrochloric and acetic. The action upon the iron was observed to be slow. After three months of contact, the external appearances were not changed. The acids were replaced by the same solutions and this procedure repeated for two years. After this period, changes were observed to have taken place in all the cubes and the penetration was complete. The cubes of cast iron which originally weighed 15.324 grammes each, weighed only 3½ grammes after this period of two years in acetic acid. This acid had been found to have been the most energetic. The values for other acids were not given.

Davy[104] observed that a piece of iron chain exposed to the action of sea water and originally weighing 14 pounds 5 ounces lost 70 grains after a period of 24 hours.

Bauerman[105] writing on the porosity of rust, called attention to a great increase of volume accompanying the change of iron into rust. He observed that a unit of malleable iron produced ten times its volume of rust. He did not state how he had arrived at this value.

These are all illustrations of examples under a wide variety of circumstances and environmental conditions, consequently, little would be gained by any comparison.

3.1.3. Varieties of rust

Mallet observed that in some cases of corrosion in sea water, the surface of the iron remained perfectly bright and clean though the metal

was gradually dissolved. In river water he found that in many cases the rust formed a firmly adherent crust, while often it was of the usual loose brown or reddish - brown powder. Another variety, to which Mallet gave the name of 'tubercular corrosion,' and to which Jamieson[107] also referred, was due to irregularity in the composition of the original metal, or to local conditions of the metallic surface when the rusting was confined to special points of the surface. The result was the formation of little mounds of rust, with 'pitting' of the metal underneath.

Cushman[108] was probably the first to comment on these pits in any detail when he observed that two kinds of mounds of rust could be seen, one being in the form of a little hillock, more like a 'sugar loaf' in shape, while the other was like the crater of a volcano. He considered that the probable explanation lay in the different local electrical conditions, depending upon whether the central portion was electro-negative or electro-positive to the surrounding area.

3.2. COMPETING MATERIALS

3.2.1. Phillips' detailed accounts

At the time when Mallet was carrying out his extensive range of experiments (1836 - 1842) steel was not in wide use as a constructional material. With the development of steel in the middle of the nineteenth century, however, the comparative endurance of steel and iron when exposed to corrosive influence became of major importance.

Phillips appears to have been the first to have given serious consideration to this in 1880. He remarked:-[109] [110]

"Having regard to the numerous discussions which have taken place during the last three years respecting the materials best suited for the construction of ships, boilers and bridges, and remembering the efforts that have been made to perfect mild steel for those purposes, it is extraordinary that the subject should have received so little attention."

From these remarks, it can be seen that the familiar pattern re-emerges, of a material being selected and used with little consideration

given to its corrosive resistance prior to service. Mallet carried out his series of experiments long after the various materials had been in service and this same sequence applied to Phillips' work.

In this work, he observed the action on these metals when exposed to similar influences.

He had six sets of tubes of different brands of iron and steel prepared for the purpose and tested them in a special apparatus in Sheerness Dockyard. (Fig 3a.)

These appear to have been the first corrosion testing rig details to have been published.

Altogether, the total number of tubes tested was thirty eight, eighteen being of iron and twenty of steel.

Some of the tubes were cold drawn and the others were welded. The cold drawn tubes had originally a smooth and clean surface with only a film of oxide, the result of annealing, whilst the welded tubes, especially the iron ones, were rather rough with the usual oxide coating. This would be in favour of the steels in calculating the losses of weight. All the tubes are recorded as being carefully weighed before and after each experiment, and were 8ft. in length and 2½ inches in diameter, representing an exposed surface inside and out of 9.58 square feet. Some of the tubes Phillips designated as 'ordinary tubes' and do not appear to have been prepared in any way. They were 2 inches in diameter, and had 7.68 square feet of exposed surface.

Fig. 3b illustrates the general layout of the testing apparatus. It consisted of two cylinders, 3ft 7 inches in diameter and 6ft in height. The tubes were screwed tightly through the top ends. The lower parts of the tubes, 5ft 8 inches in length, were fixed in the cylinders and filled with various kinds of water. They were exposed to an average steam pressure of 50 lbs per square inch. The upper parts represented the steam spaces of boilers and were enclosed in a chamber open to the air and supplied

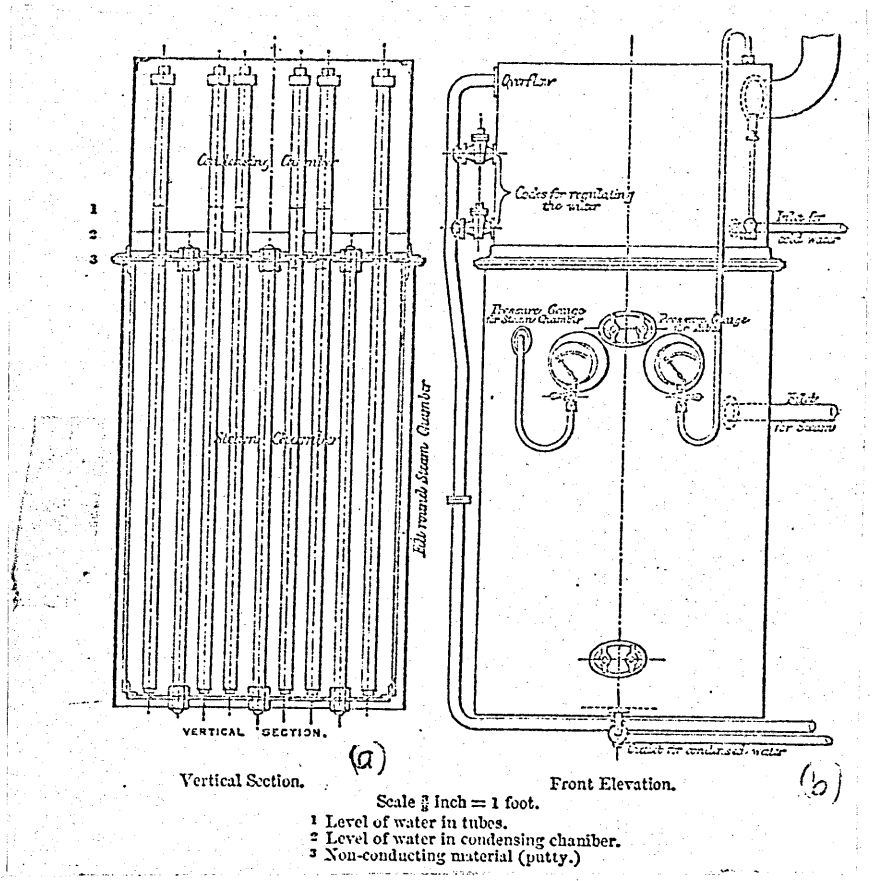


Fig. 3 THE FIRST DETAILED DIAGRAM OF COMPLEX CORROSION TESTING EQUIPMENT(120)

with sufficent cold water to ensure partial condensation of the steam within. The average steam pressure in the tubes was about 38lbs per square inch.

Fig. 4 gives detailed results of the tests after a period of two years.

The results show conclusively that the corrosion resistance of the iron was greater than that of the steels tested.

The importance of this work is increased because Phillips gives a much clearer insight into the way he carried out his testing procedure than former workers.

By illustrating his testing rig, a much deeper understanding can be obtained from the results he obtained. By stating the physical dimensions of the tubes and rig the validity of these results can be investigated.

Phillips states that each of the tubes was 8ft in length and 2½ inches in diameter and the ends were to be screwed into position. After a period of some two years, within a corrosive environment, there would be a great tendency for at least one of the nuts to be rusted and very difficult to remove without excessive pressure. This would require considerable vibration in the effected tube resulting in an unknown amount of corrosion product falling away.

Yet in his analysis, Phillips states the results to within an accuracy of one hundreth of an ounce.

The physical size of these tubes and the difficulty of access, as illustrated in the diagram, also must have involved considerable loss of corrosion product in varying degrees as the tubes were manhandled from the rig and yet Phillips gives no indication that the tubes were steamed after the test and a net weight loss determined by this method.

The margin of error from these causes however, is not sufficient to significantly effect Phillips' results and conclusions.

—	Kind of Water, Alkali, &c., in Tubes.				Loss of Weight.			
	Set 2. ½% Density and 500 grs. of Lime; Air admitted Weekly.	Set 3. Sheerness Well, no Alkali; Air admitted Weekly.	Set 4. Rain, and 500 grs. of Soda; Air excluded.	Set 5. Distilled from Sea Water, no Alkali, Air excluded.				
Tubes.	Loss of Weight.	Loss of Weight.	Loss of Weight.	Loss of Weight.	Total Loss of Weight.	Mean Loss per Tube.	Average Loss per Sq. Ft. of Surface.	Average Loss per Sq. Ft. of Surface.
	Oz.	Oz.	Oz.	Oz.	Oz.	Oz.	Oz.	Grs.
Steel B.W.	21·25	28·00	20·25	11·25	80·75	20·19	2·1072	921·90
,, B.F.	24·00	27·25	15·75	12·50	79·50	19·87	2·0746	907·63
,, C. .	23·75	23·00	22·00	13·25	82·00	20·50	2·1398	936·16
,, F.F.	21·25	16·50	17·00	18·25	73·00	18·25	1·9050	833·43
,, G. .	20·25	16·25	18·75	16·50	71·75	17·94	1·8723	819·13
Total loss	110·50	111·00	93·75	71·75	387·00	..	..	169,312·50
Mean loss	22·10	22·20	18·75	14·33	19·35	..	2·0197	883·66
Iron A.I. .	12·75	11·75	14·50	13·25	52·25	13·06	1·3635	596·53
,, D. .	15·50	16·00	17·25	12·25	61·00	15·25	1·5918	696·41
,, E. .	14·00	17·25	25·25	12·00	68·50	17·12	1·7876	782·07
,, F.s. .	6·00	7·00	5·00	3·75	22·25	5·56	0·7113	311·19
,, A.Y.	14·25	11·50	..	..	25·75	12·87	1·3440	588·00
Total loss	62·50	63·50	62·50	41·25	229·75	..	..	100,515·62
Mean loss	12·50	12·70	15·62	10·31	12·77	..	1·3890	607·71

(120)

Fig. 4 PHILLIPS' COMPARISONS OF STEEL AND IRON

Apart from tubes, Phillips tested a series of small discs of iron and steel of various brands in the test rig. There was a striking difference found between the discs regarding the nature and severity of the corrosion.

He gives no details of the method of suspension but states that while a disk O (steel) was very uniformly affected, a disc V was deeply pitted, yet the loss of weight in the latter was 19 grains less than in the former. The O2 disc from the same plate O disc was much rougher, while the loss of weight was 18.8 grains less. A disc 'a' (steel) was peculiarly affected, being pitted in small deep holes whilst the intervening surface was scarcely touched. Again the edges of some of the discs were corroded uniformly. The edges of the 'r' iron discs were corroded in ridges and grooves.

The variety in the manner of corrosion could be attributed to a number of causes. The different edge effects would probably be due to the stresses set up during specimen manufacture and preparation. If the discs were produced by a punching operation then high stresses would be set up in the region of the edges. A slight projection on the base of the punch would produce a stress raiser at the position of impact on the material from which the disc was being produced. This would tend to cause corrosion in the form of ridges and grooves.

The lack of homogeneity in the material could have caused pits to form in some specimens.

The position of the specimens in the rig may have influenced the varying rate of overall corrosion.

3.2.2. Steel producers press their case

Regarding the relative merits of cast iron and steel in their resistance to corrosion, not all workers would agree with Phillips' results.

Siemens[19] described how, for some years, his chemist, Willis, had conducted a series of experiments at Landore.

In one series, extending over six months, made partly in a boiler supplied with salt water, and partly by exposure in a tidal river - the plates were exposed to the air for six months, and then immersed for six hours in salt water. The result was in some instances of open exposure, slightly in favour of iron, but in the cases of boilers, always very much in favour of steel. A point which Willis had emphasised, was the importance of having a surface as perfectly clean as possible. He had found that by carefully cleaning the surfaces of oxide by dipping the plates in the first instance in an acid solution, the corrosion was greatly diminished.

This fact had already been stated by Barnaby,[111] when he showed that the magnetic oxide scale was very deleterious in its effects.

Siemens had a vested interest in promoting the advantages of steel, being a major producer, and to what degree one can trust the scientific honesty of his chemist is difficult to judge, especially when no detailed evidence was supplied. Steel had been used some twenty years previous to this for the construction of ships and boilers but had received bad publicity on the grounds of poor corrosion resistance, and its degree of popularity had considerably waned.

A source of evidence concerning this was given by Martell:-[112]

"Many shipowners were anxious to build ships of steel, but an opinion was abroad that it deteriorated more quickly than iron, hence the importance of having reliable facts upon which to form a correct opinion on that branch of the subject. _ _ _ "

The report published by Phillips also caused a certain degree of consternation in the Admiralty, since by 1881 they had replaced many of the cast iron boilers with shell steels.

Barnaby,[113] who was possibly instrumental in this change, being an Admiralty Inspector, also made a challenge to Phillips' work considering in fact that there was no considerable difference between the corrosion rates of cast iron and mild steel. However, like Siemens, he had a vested interest being possibly responsible for this change and also like

Siemens, he did not produce any scientific evidence to back his views.

Another prominent steel producer was Bessemer,[114] who remarked that one of his customers had told him;-

"The six boilers of your steel, made twenty-two years ago, are still in use, and have no appearance of corrosion."

He considered that this was sufficient evidence that he could give to show that Bessemer steels and similar grades of mild steels, gave good service.

3.2.3. Parker extends Phillips' range of experiments

Shortly after Phillips carried out his series of experiments in 1880,[115] Parker carried out a series of experiments with a similar range of materials under a variety of conditions.

He obtained 12 discs, 4½ inches diameter and about ¼ inch thick from each of 12 manufacturers of iron and steel. Six of the discs from each maker were machined bright entirely to remove all scale and the other six were turned round the edge only, so as to damage the scale as little as possible. They were divided into six series, each containing twenty-two discs, one black and one bright from each of the works and were fixed together as illustrated in fig 5; the plates being separated from each other by means of glass ferrules about ¼ inch long and 1 inch diameter, in an attempt to isolate each disc and prevent galvanic action between them. This was one of the precautions that Phillips in his range of experiments failed to take.

Parker immersed one of these insulated discs in sea-water, and it was found that by completing the circuit between any two of them, a galvanic current was set up.

One series (A) was suspended on the roof of a building in the city of London, exposed to the action of the atmosphere from the 13th February, 1879 to 13th May 1880, a period of 455 days.

Another set (B) was securely fixed under water to the pier at

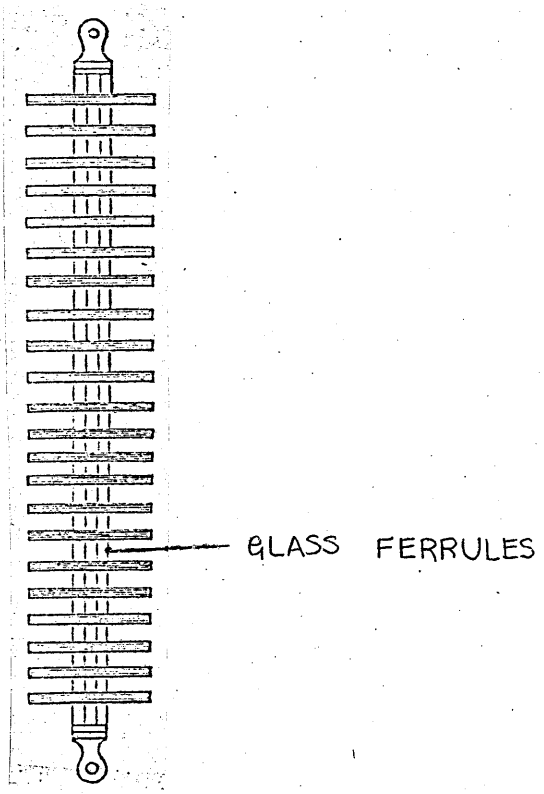


FIG. 5 SERIES OF 'BLACK' AND 'WHITE' DISCS.(115)

Brighton from 24th February, 1879 to 7th May, 1880, a period of 437 days.

A third series (C) was so secured to the engine-room floors of a ship trading to the East and was freely exposed to the action of the bilge waters, from 9th June, 1879 to 6th February, 1880, or 240 days.

The remaining three sets (D, E and F) were hung up in the wide waterspaces between the tubes of machine boilers in such a manner that they could not swing about, and were kept about 12 inches below the water-line. These three sets were installed in different vessels. The immersion lasted from the 15th February, 1879 to the 6th June, 1879 and from the 14th June 1879 to 16th February 1880, i.e. 361 days.

Parker stated that after completion of the exposure, the scale and rust were removed as carefully as possible by scraping and brushing the discs with a file card, and each one was then carefully weighed. Neither Mallet nor Phillips gave such detail of the procedure they took after exposure and consequently the historian in these cases is in difficulty when he endeavours to compare their work, since there is uncertainty to the degree of cleaning used. These factors are particularly important when results are given to within a fraction of an ounce.

In his results, fig. 6, the table gives the loss of metal per square foot per annum. These he obtained by dividing the total loss of weight of each disc by its area.

3.2.4. Analysis of Results

Fig. 8 results he compiled from fig 6 by dividing each of the losses in the different columns by the loss of the respective Lowmoor plates, so that different sorts of iron and steel could be readily compared. Under the heading of 'cold water' it can be seen that although the average loss of steel is a little greater than that of iron, the difference is so slight that for practical purposes it is safe to assume that bright steel, exposed to sea or bilge water, corrodes no faster than bright iron.

When exposed to the atmosphere, although there is no great difference

	Cold Water.		Atmosphere, London.	Boilers.		
	Sea. B.	Bilge. C.	A.	Zinc in Boiler. D.	Collier Boiler. F.	P. and O. Boiler. E.
Parkhead common iron .	·190	·415	·156	·058	·566	·195
Skerne common iron . .	·137	·556	·151	·062	·485	·203
COMMON IRON MEAN	·163	·485	·153	·060	·525	·199
Leeds forge best iron . .	·168	·475	·169	·061	·609	·164
Taylor's best iron . . .	·198	·527	·155	·066	·657	·191
Bowling best iron . . .	·225	·518	·150	·052	·598	·193
Farnley best iron . . .	·173	·573	·167	·069	·708	·217
Lowmoor best iron . .	·212	·539	·166	·087	·597	·209
BEST IRON MEAN	·195	·526	·161	·067	·633	·194
Landore mild steel . .	·208	·480	·206	·120	·666	·234
Brown & Co.'s mild steel .	·215	·560	·254	·147	·755	·310
Bolton Co.'s mild steel . .	·198	·544	·214	·117	·785	·250
Steel Co. of Scotland's mild steel	·207	·509	·222	·132	·739	·253
MILD STEEL MEAN	·207	·523	·224	·129	·736	·262

FIG. 6 WT. LOSS DUE TO CORROSION IN POUNDS/SQ. FT. PER ANNUM UNDER A VARIETY OF CONDITIONS(115).

between the common and the better grades of iron, the steel appears to have lost considerably more than either Lowmoor or any other iron, and the same is the case with those discs exposed to the action of boiler water with or without zinc. But although the absolute losses of both iron and steel are least, the relative differences of losses of steel and iron are greatest in the boiler in which zinc is used, there the steel lost 50 per-cent more than Lowmoor iron, Lowmoor iron 50 per-cent more than Bowling iron. These favourable results for Lowmoor are in agreement with Mallet's observations.

In fig. 8 column 9 it can be seen that the steel, with one exception had on an average, corroded only about 14 per cent more than Lowmoor iron. These experiments tend to confirm that bright mild steel corrodes faster than iron and opposed the generalised views of steelmakers Siemens and Bessemer.

Considering conditions under which marine boilers operated however, the difference was not marked and consequently the superiority of iron to steel was not established beyond doubt.

The discs suspended in the boiler of the steam vessels were found to be roughly and irregularly corroded and also deeply pitted. This agrees with the findings of Phillips' who experimented under similar conditions. Some of the pits observed extended to a depth of $^{1}/_{16}$ inch.

Concerning figs. 7 and 8 which could trace the relation of the different impurities contained in commercial iron and steel; these would be of great interest, but the rate of corrosion shows considerable variation even within the same series and with the amount of impurities small, so that it is difficult to determine with any exactness, the effect of the different elements.

A comparison of the densities and the corrosion shows the very reverse of what might have been expected from Mallet's experiments, for although there is no observable relation in series B and C, it appears

Description of Metal.	Manganese.	Carbon. Colour Test.	Sulphur.	Phosphorus.	Silicon.	Copper.	Cobalt and Nickel.	Density.
Parkhead common iron . .	trace.	·09	·027	·316	·020	·000	·15	7·618
Skerne common iron . .	·01	·10	·027	·193	·100	·021	...	7·703
Taylor's best iron . . .	trace.	·12	·005	·136	·013	·00	·05	7·745
Leeds Forge best iron . .	·03	·14	·028	·085	·110	·031	...	7·764
Bowling best iron . . .	trace.	·11	trace.	·101	·100	·016	...	7·791
Farnley best iron . . .	·01	·11	·012	·096	·090	·016	...	7·779
Lowmoor best iron . .	·01	·10	·022	·142	·120	·022	...	7·689
Landore mild steel . .	·64	·18	·074	·077	·013	·015	...	7·861
Brown & Co.'s mild steel .	·11	·12	·077	·056	trace.	trace.	...	7·854
Bolton Co.'s mild steel . .	·52	·19	·068	·041	·060	trace.	...	7·849
Steel Co. of Scotland mild steel	·26	·10	·035	·057	·032	trace.	...	7·872

FIG. 7 ANALYSES AND DENSITIES OF THE RESPECTIVE MATERIALS FROM WHICH DISCS WERE MADE.(115)

	Cold Water.			Atmosphere, London.	Boilers.				MEAN OF COLUMNS 1,2,4,5,7 & 8
	Sea. B.	Bilge. C.	Mean of B, C.	A.	Zinc in Boiler. D.	Mean of F, E.	Collier Boiler. F.	P. & Boiler E.	
Parkhead common iron	·90	·77	·83	·94	·67	·94	·95	·92	·86
Skerne common iron .	·64	1·03	·83	·91	·72	·89	·81	·97	·85
Leeds forge best iron .	·79	·88	·83	1·01	·70	·90	1·02	·79	·86
Taylor's best iron .	·93	·98	·95	·93	·76	1·00	1·10	·91	·90
Bowling best iron .	1·06	·96	1·01	·90	·60	·96	1·00	·92	·91
Farnley best iron .	·82	1·06	·94	1·00	·79	1·11	1·19	1·04	.98
Lowmoor best iron . .	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00
Landore mild steel .	·98	·89	·93	1·24	1·38	1·12	1·12	1·12	1·12
Brown's mild steel .	1·01	1·04	1·02	1·52	1·69	1·37	1·27	1·48	1·33
Bolton mild steel .	·93	1·01	·97	1·28	1·35	1·25	1·31	1·20	1·18
Steel Co. of Scotland mild steel .	·97	·94	·95	1·33	1·52	1·22	1·24	1·21	1·20

FIG. 8 COMPARATIVE LOSS OF IRON AND STEEL TAKING LOSS OF LOWMOOR IRON AS STANDARD.(115)

that in the other cases, the densest metal had corroded the fastest.

Regarding the corrosion of the black discs, Parker recorded that the least scale had come off those discs immersed in the sea, i.e. about 30% (Fig. 9); next comes the series D, which was exposed in the boiler containing zinc, with 50 per cent, followed by the two sets exposed to the atmosphere and in the bilges with an average of 70 per cent, while the plates in the boiler of the 'P and O' steamer lost 95 per cent.

With the help of Fig. 9 and ascertained loss of each black sample and the losses per annum per square foot of bright samples it is possible to compare the average depth of corrosion of the bright discs and that of the black discs where the scale had been removed. Parker did this as shown in Fig. 6.

Comparing Figs. 9 and 10, it can be seen that the black discs lost the least scale and corroded to a greater depth than the corresponding bright discs.

Parker observed this and considered it to be due to the galvanic action that had been set up.

	Cold Water.		Atmosphere. London.	Zinc in Boiler.	Hot Water.		MEAN OF COLUMNS 1,2,3,4
	Sea. B.	Bilge. C.	A.	D.	Collier Boiler. F.	P. & O. Boiler. E.	
Parkhead common iron	·70	·80	1·00	·60	1·00	1·00	·77
Skerne common iron	·30	·50	·90	·50	1·00	·90	·75
Leeds Forge best iron	·45	·85	·85	·80	1·00	1·00	·79
Taylor's best iron	·25	·50	·70	·30	1·00	·90	·44
Bowling best iron	·50	·90	1·00	·70	1·00	·95	·77
Farnley best iron	·30	·80	·95	·80	1·00	1·00	·71
Lowmoor best iron	1·00	1·00	1·00	·95	1·00	·98	·99
Landore mild steel	·30	·60	·50	·35	1·00	·90	·42
Brown's mild steel	·50	·80	·97	1·00	1·00	...	·82
Bolton mild steel	·15	·80	·50	·70	1·00	1·00	·54
Steel Co. of Scotland mild steel	·40	·80	1·00	·70	1·00	1·00	·72
MEAN LOSS OF SCALE DUE TO STAMPING AND EXPOSURE (EXCLUSIVE OF LOWMOOR IRON)	·38	·73	·74	·54	1·00	·96	

FIG. 9 RATIO OF UNPROTECTED METALLIC SURFACE OF BLACK DISCS TO TOTAL SURFACE AFTER EXPOSURE. (115)

	Cold Water.		Atmosphere, London.	Zinc in Boiler.	Hot Water.	
	Sea. B.	Bilge. C.	A.	D.	Collier Boiler. F.	P. and O. Boiler. E.
Parkhead common iron	1·2	·9	1·1	1·8	·9	1·0
Skerne common iron	3·3	1·2	·8	2·1	1·0	·5
Leeds Forge best iron	2·4	1·0	·8	1·6	1·0	·8
Taylor's best iron	3·1	1·1	·8	3·1	1·1	·6
Bowling best iron	1·8	·8	1·0	2·5	1·1	·9
Farnley best iron	3·0	·5	·9	1·3	1·0	·9
Lowmoor best iron	·9	·9	1·1	1·3	1·1	·9
Landore mild steel	3·0	·9	·7	1·8	1·2	·9
Brown's mild steel	1·8	·9	1·0	·9	1·0	...
Bolton mild steel	·6	·6	·5	1·0	·9	·9
Steel Co. of Scotland mild steel	2·2	·8	1·1	1·1	1·0	1·1

(115)

FIG. 10 RATIO OF AVERAGE DEPTH OF CORROSION OF BLACK DISCS TO BRIGHT DISCS.

CHAPTER 4

SPECIFIC CASES OF CORROSION OF IRON AND STEEL

4.1. BOILERS

4.1.1. Introduction

Of the aspects of corrosion observed during the nineteenth century, those associated with boiler corrosion received the most systematic and exhaustive investigations. The main reason for this was that corrosion was one of the causes of boiler explosions. These caused many deaths during this period.

On analysing the various investigations carried out under a variety of conditions, it is found that the forms of corrosion of boilers can be divided into three main classes:-

Furrowing,[116] [117] which is a specific form of internal corrosion;[25] secondly, internal corrosion which usually takes the form of pits or general wasting of the material and thirdly, external corrosion. These cases will be later considered separately.

Fig. 11 illustrates that furrowing is associated with high cylinder pressure and when compared with Fig. 12 shows that this form of corrosion very often took place in railway engine boilers. The incidence of explosions from this source was infrequent ranging from 0 to about 10% of boiler explosions. (Fig. 12). However, the significance of this form of corrosion was that devastation could be caused on a much larger scale due to the high pressures involved and also the lack of understanding of its cause.

Internal corrosion usually took the form of pits or the general wasting of the material over a period of years. Fig. 11 illustrates that explosions from these sources were in general occurring at lower boiler pressures. It can be seen from the diagram that there was a tendency towards the end of the century for boilers to be operated at higher pressures. Fig. 12 illustrates that there was a percentage increase in explosions due

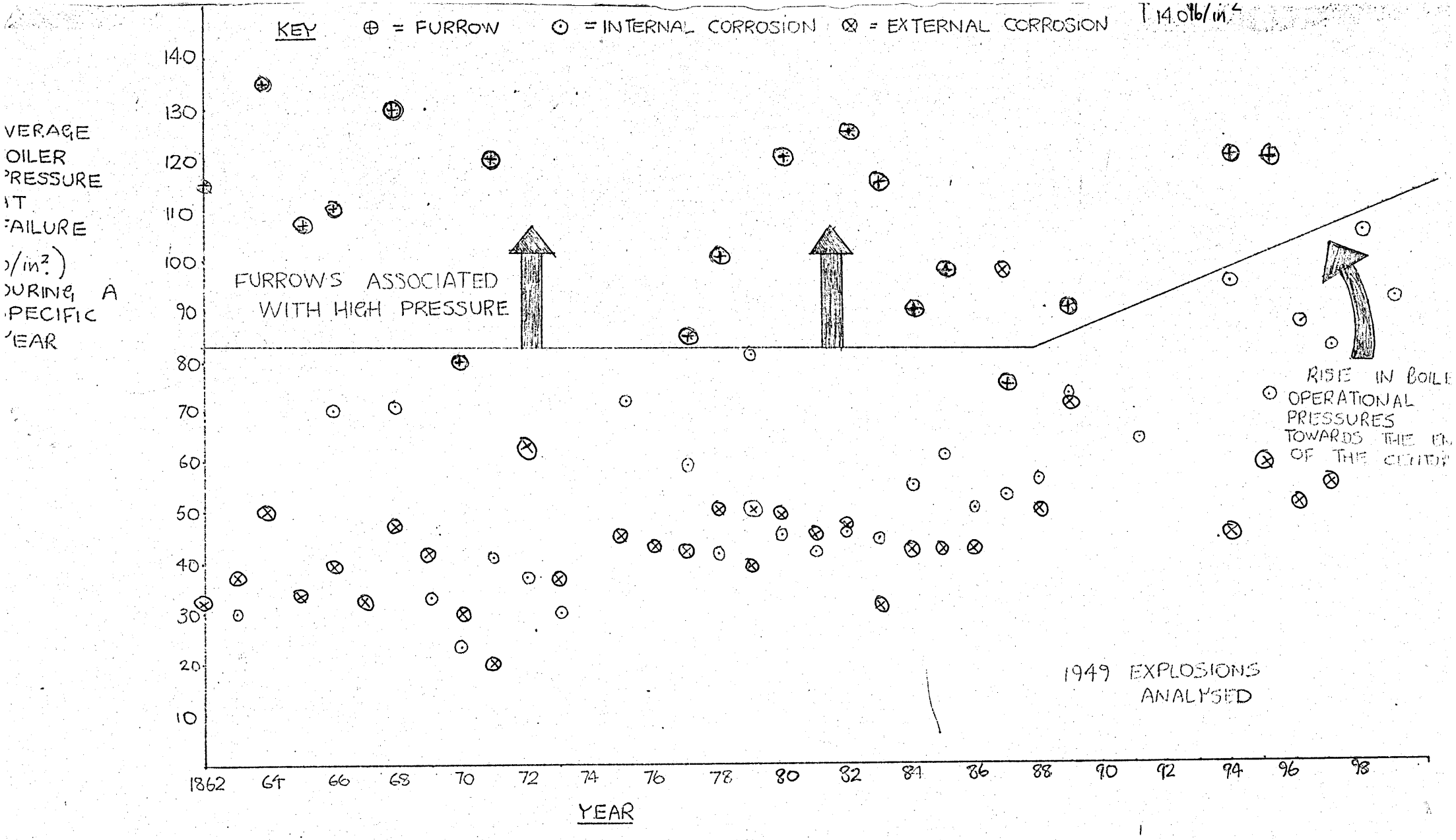

KEY ⊕ = FURROW ⊙ = INTERNAL CORROSION ⊗ = EXTERNAL CORROSION
VERAGE
OILER
RESSURE
T
AILURE
)/in²)
URING A
PECIFIC
EAR
140
130
120
110
100
90
80
70
60
50
40
30
20
10
FURROWS ASSOCIATED WITH HIGH PRESSURE
RISE IN BOILE
OPERATIONAL
PRESSURES
TOWARDS THE EN
OF THE CENTUR
1949 EXPLOSIONS ANALYSED
1862
64
66
68
70
72
74
76
78
80
82
84
86
88
90
92
94
96
98
YEAR

Fig 11

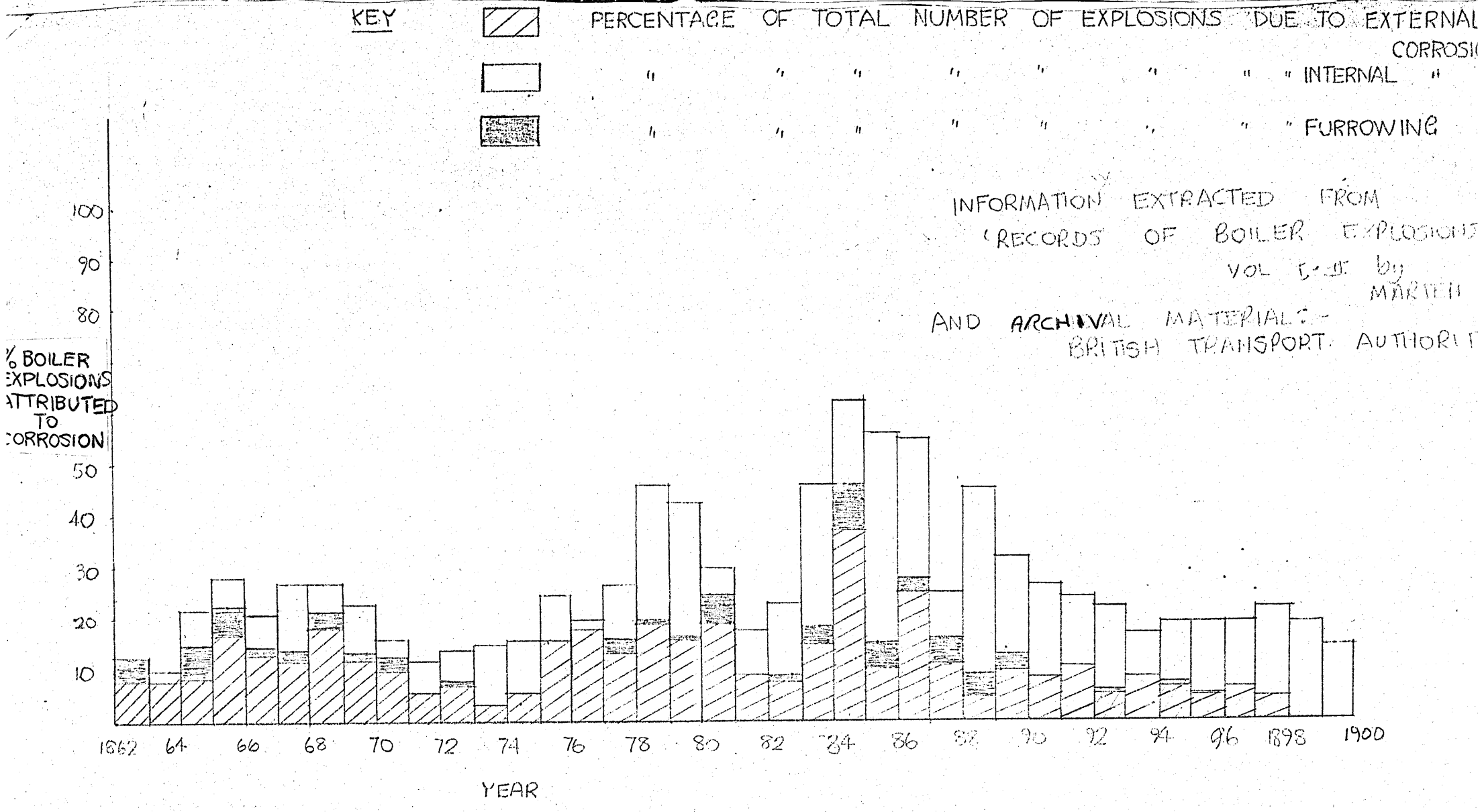

KEY
PERCENTAGE OF TOTAL NUMBER OF EXPLOSIONS DUE TO EXTERNAL CORROSION
" " " " " " " " INTERNAL "
" " " " " " " " FURROWING
INFORMATION EXTRACTED FROM 'RECORDS OF BOILER EXPLOSIONS' VOL I-II by MARTIN AND ARCHIVAL MATERIAL :- BRITISH TRANSPORT AUTHORITY
% BOILER EXPLOSIONS ATTRIBUTED TO CORROSION
100
90
80
50
40
30
20
10
1862
64
66
68
70
72
74
76
78
80
82
84
86
88
90
92
94
96
1898
1900
YEAR

FIG 12

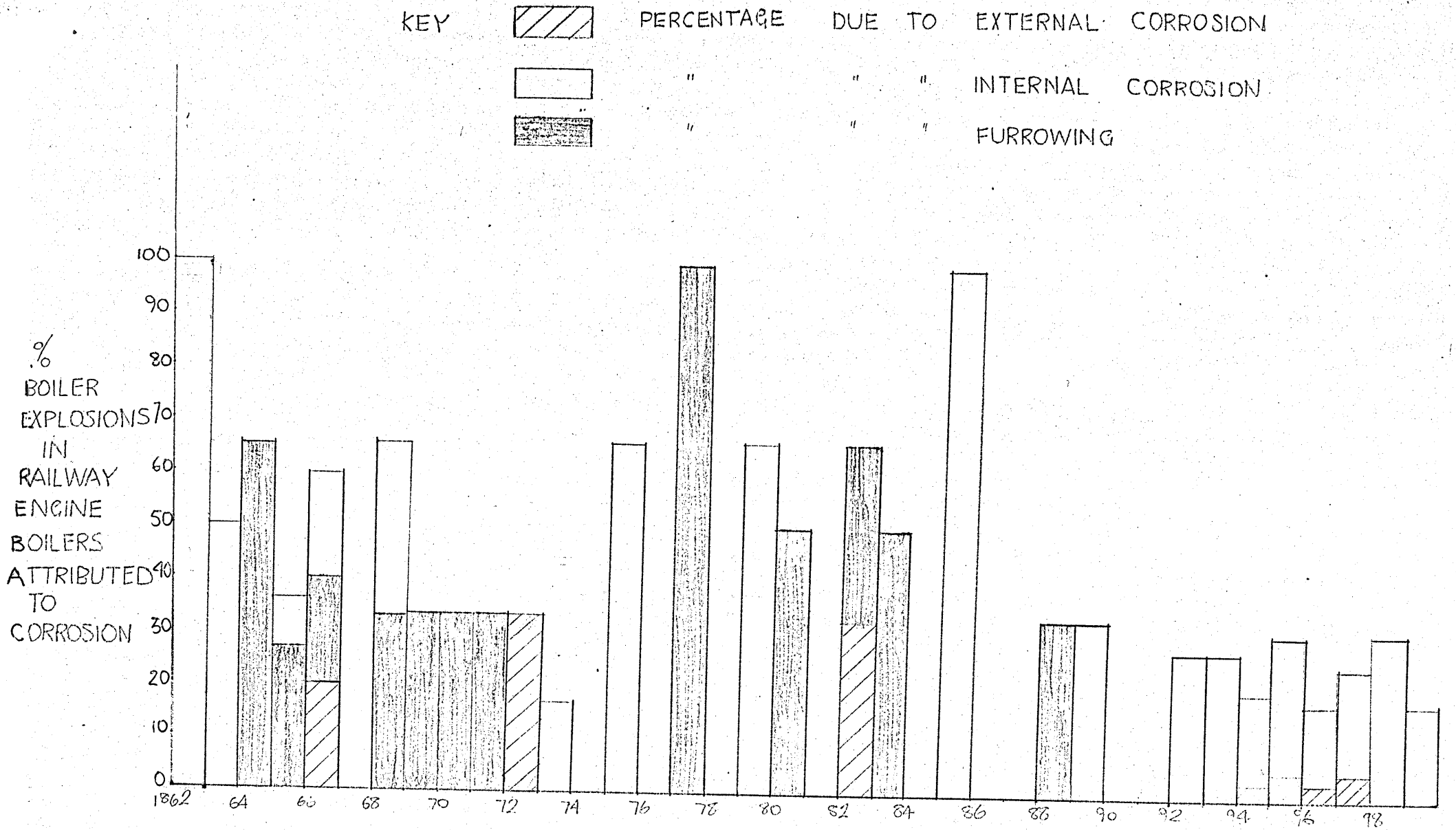

KEY
PERCENTAGE DUE TO EXTERNAL CORROSION
" " " INTERNAL CORROSION
" " " FURROWING
% BOILER EXPLOSIONS IN RAILWAY ENGINE BOILERS ATTRIBUTED TO CORROSION
100
90
80
70
60
50
40
30
20
10
0
1862
64
66
68
70
72
74
76
78
80
82
84
86
88
90
92
94
96
98
YEAR

Fig 13

DIAGRAM FROM "BOILER EXPLOSIONS"
by E.J. RIMMER
Pub. 1912.

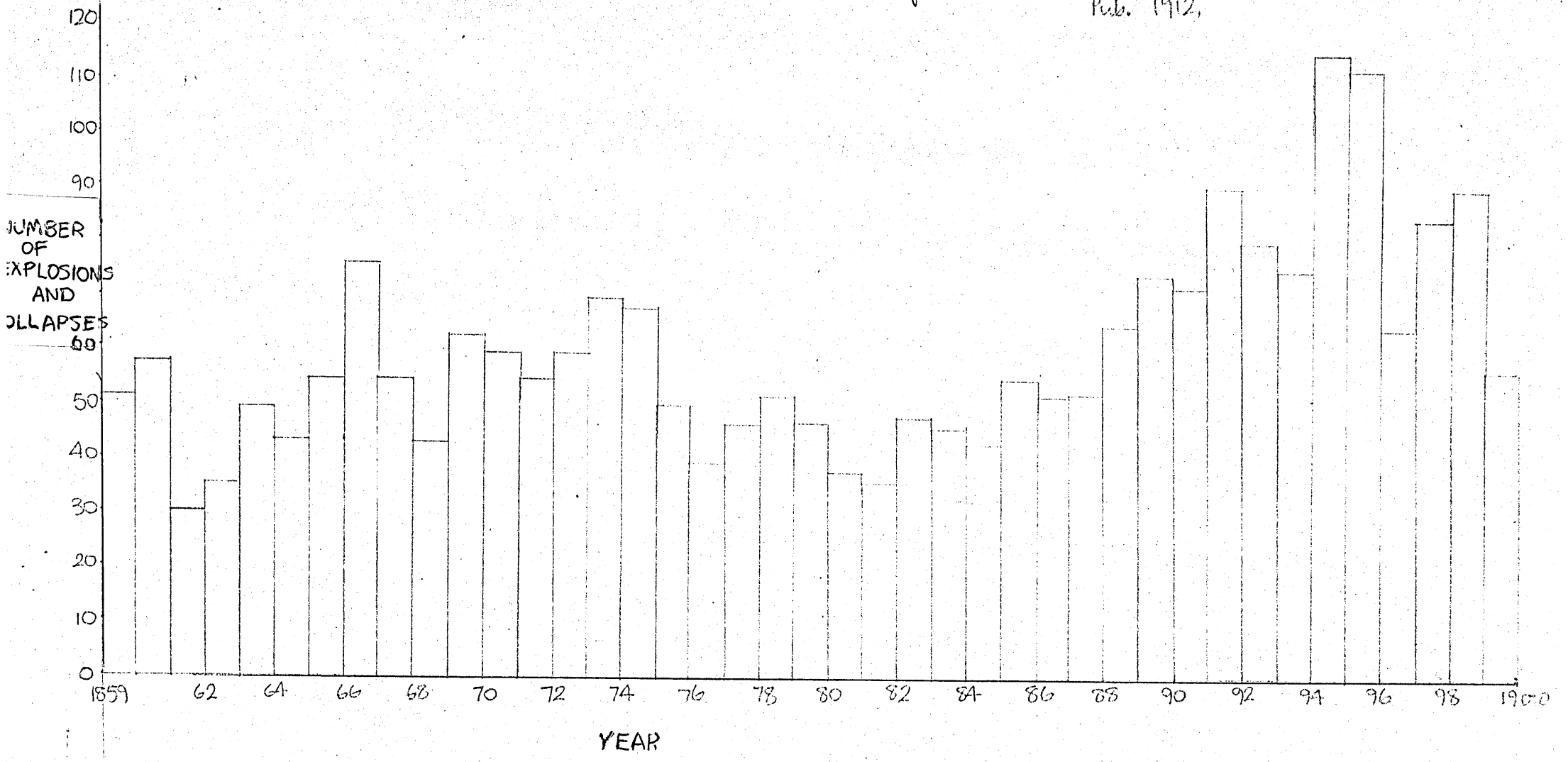


FIG 14

to internal corrosion as the century progressed. Many of these boilers had been operational for some 20 years or more and failure had occurred because the boiler skin had wasted away.

External corrosion was often due to the failure of the boiler supports and leakage from joints which could go on undetected for a considerable time. These can be seen to have occurred at boiler pressures in the range of 30 - 50 lbs/in.^{2}

The factors that accelerate the corrosion include galvanic action due to lack of homogeneity or different metals in contact; animal or vegetable grease on the plates and indentations or scratches.

4.1.2. Problems of Furrowing

In a report on an accident published in 1862 in The Engineer, in which two men were killed, on examination of the wreck of the boiler, it was found that extensive corrosion had taken place on the inside of the middle ring of plates, and near one of the longitudinal seams of rivets. The report stated:-(116)

"_ _ _ This corrosion in grooves is known as 'furrowing', and although well-defined cases of this sort are occasionally referred to as mysterious causes, there can be but very few, if any, locomotive engineers who have not had opportunities for observing the phenomenon itself. We have ourselves seen, on several of our great lines, (railway companies) boiler plates otherwise apparently sound, but with a long deep groove - almost resembling the cut of a square-nosed tool, half an inch or so from a rivetted joint."

The 'furrowing' referred to was a form of internal corrosion which was found to be a frequent cause of boiler explosions, especially in locomotive boilers.

It can well be appreciated that corrosion in this form would rapidly cause plate failure. It occurs where there is a sudden change of thickness either along the lines of the seams, or opposite the edge of angle-iron

attachments. It is still a major cause of failure and is a form of stress-corrosion. The variation in pressure and temperature causes strains in the material and consequently cracks occur which when within a steam environment result in eventual failure.

An insight into the form of inspection carried out on locomotive boilers at this time by one of the railway companies was also mentioned:-(116)

"_ _ _ We have understood, indeed, that on the Great Northern Line, it has lately become the practice, when an engine is in for repairs, to take out a few of the tubes next to the plates of the boiler, and after thrusting in a lamp on the end of a long rod to observe as far as maybe, the condition of the plates. But little could be gathered however, from such an examination."

The inference from the article was that little or no further action was taken and the engine was allowed to continue, presumably until it exploded with a consequent loss of life.

Another article appeared in the Engineer about this time,(117) which indicated that a more thorough investigation of corrosive action had taken place. H. W. Tyler was making the examination on behalf of the Railway Department of the Board of Trade. He stated:-(117)

"_ _ _ In examining the fractured portion of this boiler, I observed that corrosion had been actively going on in several parts of it, particularly above two seams of rivets and situated on the left side of the middle ring. The metal had been eaten away along a line in an irregular manner and had been reduced in places to about $^{1}/_{16}$" .

This value of $^{1}/_{16}$" wall thickness mentioned by Tyler, appears to have been a critical thickness for operating conditions of pressure at that time, since this value is mentioned at many subsequent inquests. It was obviously the critical thickness at which rupture might be expected at the ordinary working pressure of the engine, i.e. 100-120 lbs/sq"

Tyler goes on to say:-(117)

"_ _ _ The interior of the barrel had last been examined in 1857, at which time, a new set of tubes was inserted. It was said to have been in good order and was expected to outlast another set of tubes _ _ _"

It is very likely that the boiler was not examined for furrowing at the earlier date since it is difficult to believe that the reduction in plate thickness to about 1/6 of its original dimension had occured in less than six years. This fact was evident to Tyler, who suggested:-(117)

"It is necessary that inspection be carried out more frequently into the conditions of plates. When no symptoms of leakage or other indication of defect are observed, it is at present practice in locomotive works not to examine interior surfaces of barrels of engine boilers except when tubes are taken out for removal. The first set of tubes in engines lasts six years. All tubes should be taken out and a boy sent into the interior to brush away deposits formed from impurities in the water."

This was obviously a great step in the right direction, but it is probable that the boy performing the task would also be asked to look for any corrosion and it is very unlikely that he would have had the skill and experience to carry out this work.

4.1.3. Design Changes Introduced

During the period between 1857 and 1862, there was evidently a change in boiler design to overcome this problem of furrowing.(118)

"In order to remedy the tendency of corrosion along the seams of rivets it has latterly become the practice to place the upper plates inside the lower ones, instead of outside them, at the joints, a mode of construction which had not been adopted when this boiler was made (1857). It is generally believed, that by avoiding the ledge which is formed by the edge of the lower plate, when that plate is placed inside the upper one, the deposit caught by such a ledge, which promotes corrosion is deprived of its resting place. This is only a partial remedy since plates continue to be eaten away below the seam in somewhat the same way."

The reference that had been made by Tyler in 1862, to the 'ledge action' as a major factor contributing to furrowing, was again referred to four years later by Kirtley who illustrated his comments:-(118)

"In the longitudinal joints of the boiler, the grooving from corrosion is generally found to be more marked when the inside ledge of the lap faces upwards, as in E, Fig. 15, than when it is turned downwards, as at D. In the former case, it may be considered that the deposit will collect upon the projecting ledge in larger quantities, forming a thickness of deposit sufficient to be detached bodily by the springing of the plate under pressure; and it will consequently leave the bare plate more frequently and extensively exposed to the direct action of the water, than when the edge of the plate faces downwards, as at D, because in the latter case, the thinner film deposit will not be so readily and frequently detached from the plate by the same action."

In the four years that had passed since Tyler's paper, the problems of furrowing received more extensive investigation and Kirtley was able to outline the problem in a more precise way than any of the earlier investigators:-(115)

"_ _ _ In the present ordinary construction of locomotive boilers with lap joints, (as shown in fig 16,) the wear by corrosion of the plates is found principally round the smokebox end of the boiler barrel, in the interior, opposite to the edges of the outside angle iron, (as shown at AA in fig. 17) where an angular groove is found to be eaten out of the plate by corrosion."

Fig. 17 illustrates in more detail the grooves and Kirtley explains these in detail. He continued:-

"In the ordinary construction of locomotive boilers with lap joints (as shown in fig. 16) the boiler is constructed of three rings, each ring formed by two plates of 7/16 inch thick, rivetted with lap joints FF and HH. The general amount of lap is 2¼ inches for single rivetted and 3½ inches for

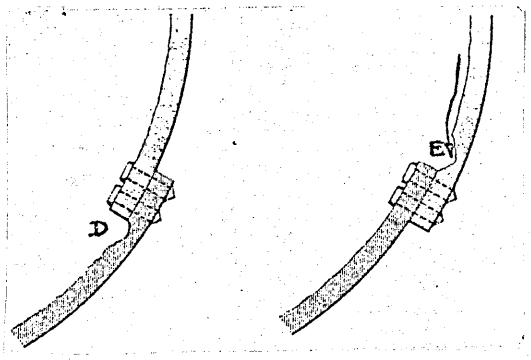
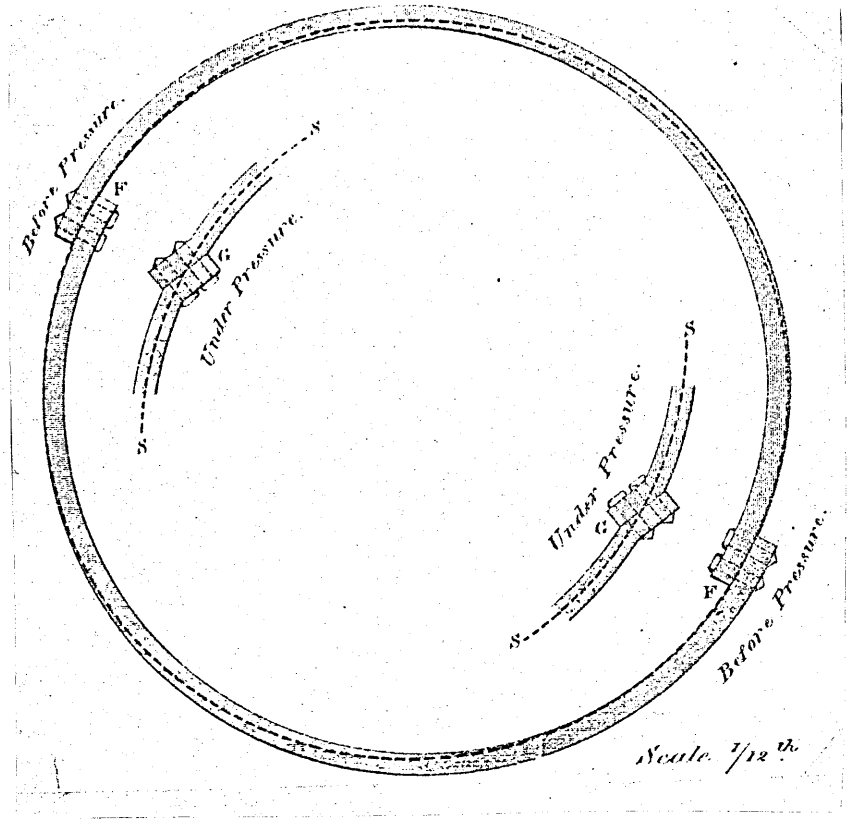
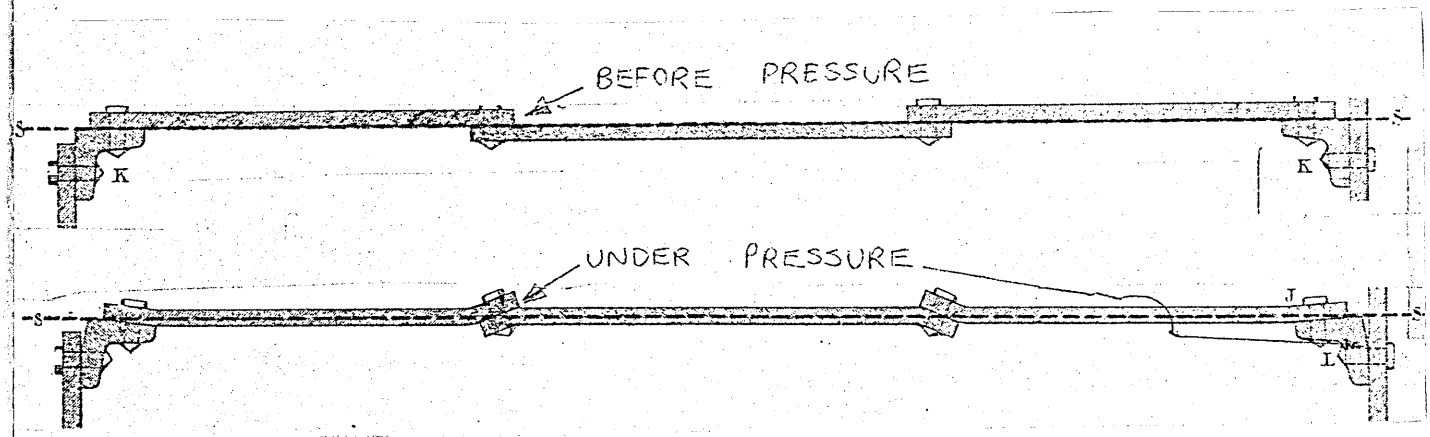


FIG. 15. GROOVING OF LONGITUDINAL JOINTS.AN ATTEMPT TO REDUCE GROOVING TENDENCIES BY HAVING THE LAP TURNED DOWNWARDS AS AT D.(118)





(118)

FIG. 16. THE INFLUENCE OF STRAIN IN A BOILER BARREL

double rivetted joints. The smokebox and firebox are each united to the barrel of the boiler by an angle iron KK (fig. 16). General experience has shown that after five or six years' wear of these boilers, the grooving action is developed at the joints and at the edge of the angle-iron rings.

Now the longitudinal strain upon the joints of boilers constructed in this manner tends to spring and bend the plates at the joints, when under pressure, in the form shown exaggerated in fig. 16. Kirtley then goes on to explain that the strain acts in the direction SS springing and bending the plates and continued:-

"_ _ _ The continued alternation of expansion and contraction in the boiler causes the scale that is deposited upon the plates from the water to be continually broken off at the edge of the joints by the mechanical action of this springing and bending of the plates at the lines of the joints; and the plates are thereby laid bare at these parts and kept continually exposed to the corroding action of the water, instead of the water by the deposited scale remaining attached to them. Though the corrosion produced by the water is slow in action but slight in effect on the rest of the boiler plates, which are protected by some deposit of incrustation remaining almost constantly upon them; it becomes very serious on an exposed surface of iron. _ _ _

"It must further be noticed that the pressure, under which the locomotive boilers are worked, is much higher than in the case of stationary boilers and the injurious action caused by the springing of the plates at the joints is therefore proportionately increased. _ _ _

"As an illustration of the effects of increased pressure in increasing the corroding action, it may be mentioned that this grooving of the plates has been found to be materially increased in amount since the working pressure of locomotives has been increased from 100 lbs up to the present 140 lbs per sq. inch.

"In the case of the boilers constructed in the ordinary manner (lap), the plates cut out show the grooving action of the corrosion below the water line, while they are comparatively clean above."

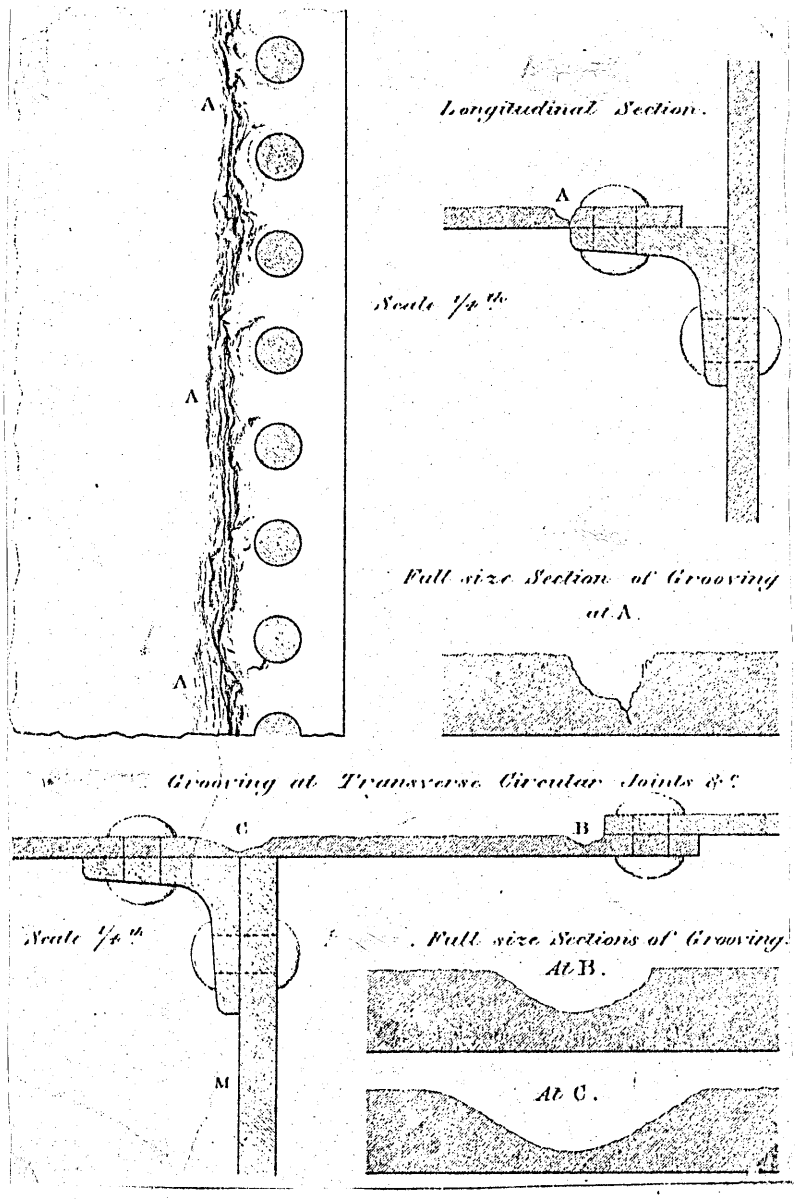


FIG. 17. GROOVING CAUSED BY CORROSION IN BOILER BARRELS WITH ANGLE-IRON AND LAP JOINTS.(118)

From these observations, Kirtley concluded that the corrosion of the plates at the joints was to be attributed to the chemical action of the water in the boiler being concentrated upon those particular parts in consequence of the mechanical stress. He was able to appreciate this because he observed that the middle plates which were relatively free from stress and only subject to chemical action showed no furrowing. Joints in the upper part of the boiler above the water line were also free from furrowing and where exposed to the mechanical action alone, without the chemical action.

Tyler[117] and later Kirtley[118] certainly had a reasonable understanding of the problem of furrowing. They failed, however, to appreciate fully that the crack itself formed a resting place on which deposits could settle. Tyler considered that the resting place had been removed with the change of construction. At this stage in the development of corrosion science, there was little appreciation of the problems of stress-corrosion and corrosion fatigue. A point of significance was that the problem was fully understood and logical attempts within the confines of their experience were being made to overcome it.

Within a few months of Tyler's paper, the Western Times of Exeter reported another boiler explosion in which:-[119]

"_ _ _ The plates near an angle-iron junction had 'furrowed' or become corroded in a deep groove, whereby the thickness had been reduced to 1/16" and finally gave way making a rent 20" x ¼" wide. No other damage was observed, 30 people were killed."

However, the Manchester Boiler Association[120] reported that they had examined 458 boilers of which 47 were badly corroded and 5 very dangerous. No accidents had occured to boilers inspected by the Association, although many others had exploded.

The following year, the incidence of boiler explosions continued. A report in The Engineer stated:-[121]

"_ _ _ There have been a greater number of boiler explosions this year than ever before. Usually about 25 explosions occur yearly in Great Britain. This year already 40 have occurred. The use of steam power is increasing and while many thousands of boilers are growing old, higher pressures are being used."

Although the regularity of boiler explosions in general increased, the number of explosions in boilers inspected by the M.S.U.A. was negligible. Consequently, the reputation of the Association increased. The inspectors' working for the Association were gaining considerable experience.

4.1.4. Apathy of boiler owners

One of the tasks that faced the inspecting organisations during the early years of their work, was to convince users that the safety of a boiler depended very largely on its construction, conditions of operation and the manner in which it was operated, and that the mysterious causes to which explosions were so often attributed were not to blame. Many boiler-users did not understand why an external examination alone was considered to be insufficient and at first only a very small proportion could be induced to provide the necessary facilities for internal examination. Their reluctance was perhaps understandable because many of them had been in the habit of working their boilers for prolonged periods without interruption and to be asked to take a boiler out of service and prepare it for both external and internal examination seemed to be a sacrifice of what was often much needed boiler capacity. It gradually became to be recognised however, that external and internal examination was essential and in time, the boiler users provided the required facilities. It became to be recognised that a thorough examination was not itself sufficient and that it required to be supplemented by an inspection under working conditions so that proper functioning of the mountings on which safety depended to a certain extent, could be verified. The task of persuading the user who was reluctant to prepare a boiler for examination was greatly facilitated

by the legislative requirements that were enacted later.

4.1.5. Inspectors' routine

The examination procedure[123] which was established in the early days of boiler inspection was first to sketch the boiler and record particulars of the mountings and other relevant data. From these particulars the safe working pressure was calculated, the conditions as revealed by the inspectors' report being taken into consideration together with any unusual features in the working conditions; in some cases, a hydraulic test or a special examination e.g. after removal of lagging and brickwork, was deemed to be necessary. If satisfactory, the boiler was then certified for the ensuing 14 months and a report was sent to the user. The boiler was subsequently inspected under working conditions and another report furnished. As each report dealt with the more important defects these were recorded along with any repairs that were made and gradually a history sheet of each boiler was built up. The work of a boiler inspector in the early days appeared to present many difficulties and hardships. Facilities for entering boilers were provided primarily to assist the work of construction, particularly riveting, and the openings appear to have been very awkwardly placed from an inspectors point of view. The treatment of feed water to reduce scale formation and minimise corrosion was in its infancy and boilers were often heavily coated with deposit, . . . while rapid corrosion, occasionally at a rate sufficient to endanger the safety of a boiler during the interval between thorough examination, was all too common. It appears that on many occasions, a boiler was taken out of commission at the close of the day preceding the one on which the examination was to take place, so that the inspector was sometimes greatly hampered in his work by excessive heat. At this time, there was hardly any local public transport and an inspector went from one appointment to another mainly on foot.

A serious difficulty that must have beset those responsible for assessing the safe working pressures of boilers when inspection first began, was the absence of reliable formulae for calculating the strength of various parts. This difficulty was of course, no different from that which arose in the design of many other structures, such as bridges and ships. Little was known of the stress systems arising in boilers and design was based largely on the results of past experience, a procedure that was essentially sound if sometimes uneconomic. This however, could prove to be an advantage in certain instances, such as furrowing, where the extra metal would serve to prolong the day when failure would occur. In time, however, practical experience with different forms of construction was translated into mathematical terms and various formulae were evolved. Many of them however, were empirical, but they enabled boilers to be designed with a reasonable degree of certainty that they would withstand the intended working conditions.

In the early days of the M.S.U.A. it became the practice for the Chief Engineer to provide his committee with periodical reports that not only gave statistical information regarding boilers under inspection and the number and types of defects revealed, but also recorded in some detail particulars of the most interesting mishaps, constructional developments, efficiency tests etc., that had taken place during the period under review. These reports feature regularly in such journals as 'The Engineer'.

4.1.6. External corrosion of bricked-up boilers

Although cases of furrowing continually appeared in reports from the Chief Engineer, there were also other interesting cases from time to time. A typical one being a report in November, 1863. A report by one inspector in 1863 stated:- (122)

"_ _ _ Instances continue to be met of serious corrosion, arising from leakage of bolted joints concealed under brickwork. Connection to boilers must be made by means of fitting blocks rivetted to the shell,

excepting only the attachments to front end plates, where they are not absolutely necessary, since the plate being flat, the joints are more easily made, while at the same time from their position any leakage occuring can easily be seen. The front end plate should be left completely open and not covered with brickwork, since leakage goes on behind undetected. If brickwork should cover the plate, corrosion could completely eat the plate away."

This form of corrosion was witnessed in 27 boilers in 1864[121] and its lack of detection was mainly due to its concealment behind brickwork. It was of particular relevance to stationary boilers. The most frequent cause, although the most easily detected, was from the joints of the fittings on the top of the boiler which were frequently attached by bolts instead of rivets.

Marten[25] observed that in many cases, the tops of boilers were corroded so thin that small holes burst through. These he found were sometimes found 'stopped' with wooden pegs or covered by screwed patches of plate.

The philosophy of so many boiler owners at this time appeared to be to endeavour at all cost to keep the boilers in service irrespective of the danger to life. There appears to have been several reasons for this attitude. The first one being the economics of maintaining full production, secondly, the lack of incentive that a statutory compensation scheme would have provided and thirdly, the attitude that accidents happened only to other people.

Marten[25] mentions that a set of boilers had been covered by arches of brickwork, built specifically to keep out all water and also set so as to touch the boilers only at intervals, leaving a space generally of a few inches. After the boiler had been operating for about seven years, the whole of the tops of the boilers were discovered to be dangerously thin, and had to be removed. The cause was leakage from the joints of fittings and seams of the boilers and issuing steam had been drawn along the space between the

boilers and the arches and escaped at a place where it had not attracted notice.

Figs 18. and 19 illustrate corrosion caused by covering the boiler with ashes to prevent the loss of heat by radiation. The rain and leakage beneath the ashes in conjunction with the corrosive matter from the ashes themselves, thinned the tops of boilers to a dangerous extent in a period of only two years. A similar effect could also be caused by sand.

Explosions were also caused from general corrosion of the boilers in the flues. In 1866, 119 cases were recorded of the collapse of internal flue tubes. A report of an explosion at Loughborough[118] in 1863 said that the bottom of the shell became ripped at the corroded part, and as the fracture continued spirally round the boiler several times nearly all the shell was peeled off(fig. 19.) The corrosion shown in fig 21. also arose from corrosion of the boiler.

4.1.7. Seam leakage

The greater part of corrosion in the side flues was caused by the leakage of seams.

The problem appeared to be that many boilers were emptied for cleaning as soon as work had finished on the Saturday night, long before the brick-work and flues had cooled. Consequently, the boiler would be at a high temperature with having no water present. The rivets could have been strained by the extra expansion and when the boiler would have been operational the seams and rivets would have leaked.

This type of corrosion was known as channeling and is illustrated in fig. 20. The diagram illustrates the effect of a jet of steam and water from the leaking rivet R, in cutting a series of channels into the plate along the course of the dotted lines EEE, and producing a hole in the plate at S.

It could be possible that this type of corrosion was the first stage in a rent or rip referred to earlier.

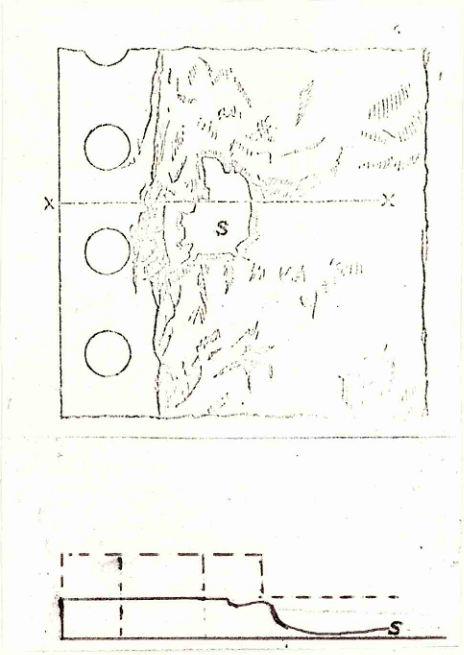


FIG. 18. AN EXAMPLE OF 'THINNING' WHICH CONTINUED UNTIL THE PLATE FRACTURED AT S.(25)

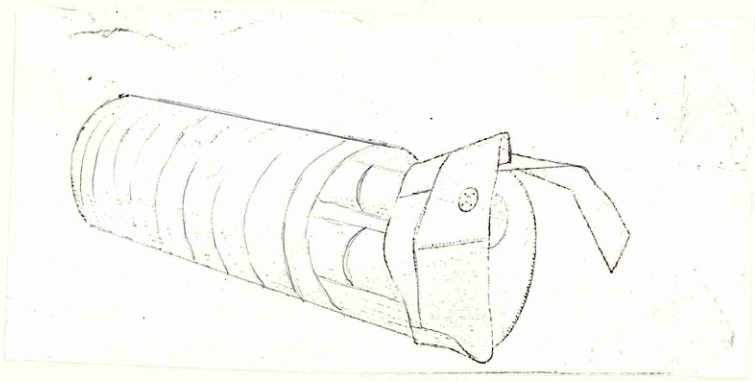


FIG. 19. RESULT OF AN EXPLOSION CAUSED FROM CORROSION AT THE BOTTOM OF THE BOILER.(25)

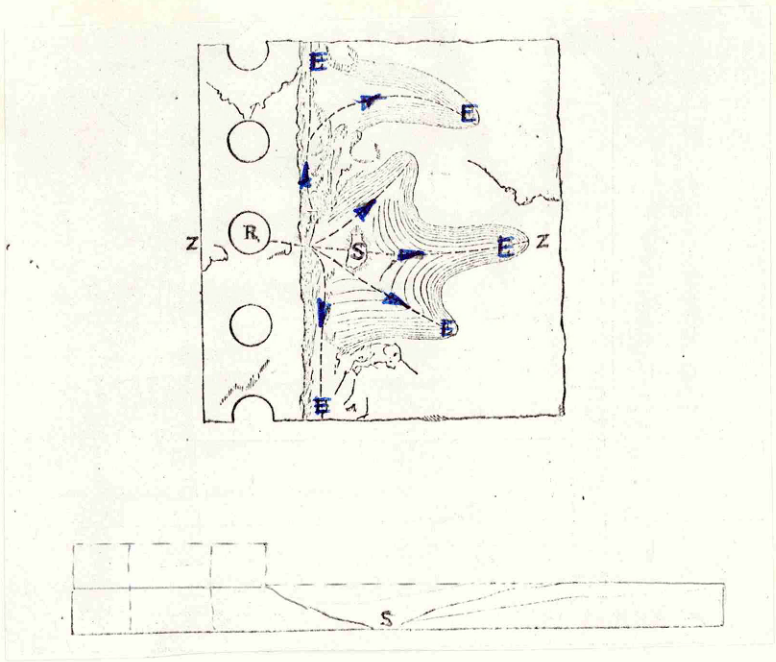


FIG. 20. SHOWS THE EFFECT OF A JET OF STEAM AND WATER FROM THE LEAKING RIVET R, IN CUTTING A SERIS OF CHANNELS INTO THE PLATE ALONG EEE, AND PRODUCING A HOLE IN THE PLATE AT S.(25)

4.1.8. Pitting

An article that appeared in The Engineer, in 1864, mentions a form of internal corrosion that had been observed during inspection:- pitting.

In the report, the usual great emphasis is placed on the problems of furrowing, but continues:-(124)

"_ _ _ In other instances, the plates become 'pitted' on their inner surfaces, as with smallpox. To compare the pits with the lunar seas disclosed in Mr. De la Rue's photographs of the moon would not do justice to the former. The iron is eaten away almost everywhere, not uniformly over the whole surface, but in numberless holes. Wherever very pure water is used, or peat water or water containing sulphur, there is some corrosion on, while, as for furrowing, there appears to be no effective precautions against it."

4.1.9. Effect of Mine Water

A diagram showing this effect is Fig. 21. The consequence of pit formation was not as destructive as that of furrowing. The greatest concentration of pits was along the part of the shell most exposed to heat and in the particular example shown, the pits did lead to a boiler explosion. The boilers had been at work sixteen years. It was reported(25) that corrosion had commenced about eight years before the explosion, when the feed water began to be extracted from some iron mines. This corrosion had been known to be going on for some years, but was not considered sufficient to cause danger. Another example exhibited by Marten was taken from the sweep plate over the fire in a plain cylindrical boiler which had been operating for ten years. There was no indication in the report that this boiler had exploded. The feed water had attacked the iron over the area DDD, where it had been unprotected by scale. The protection afforded by scale against occasional corrosive feed water can be observed. From the diagram, it can be seen that good protection had been given where the scale had not been knocked off; and the edge of the sound part projects over the hollow, as seen in the half sections Figs. 22 and 23.

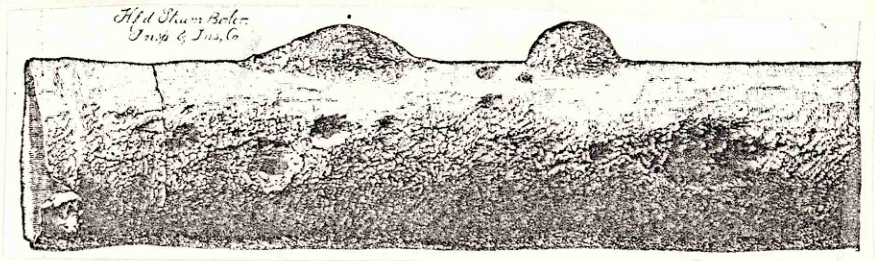


FIG. 21. A PITTED TUBE(132)

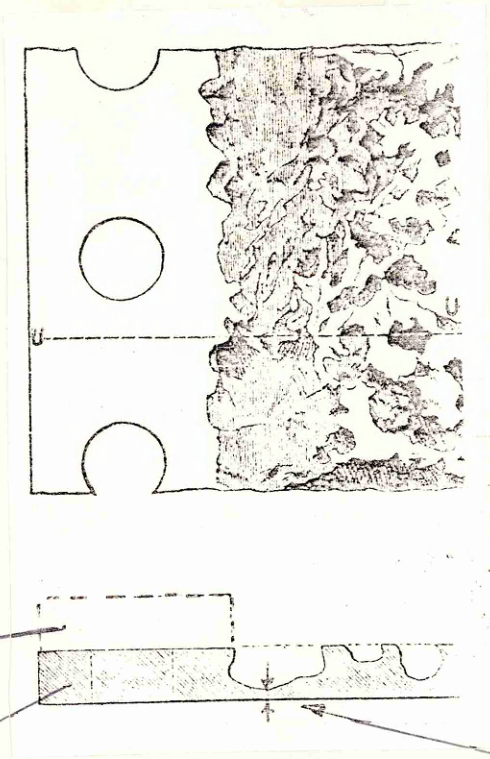


FIG. 22 A PITTED SURFACE[25]

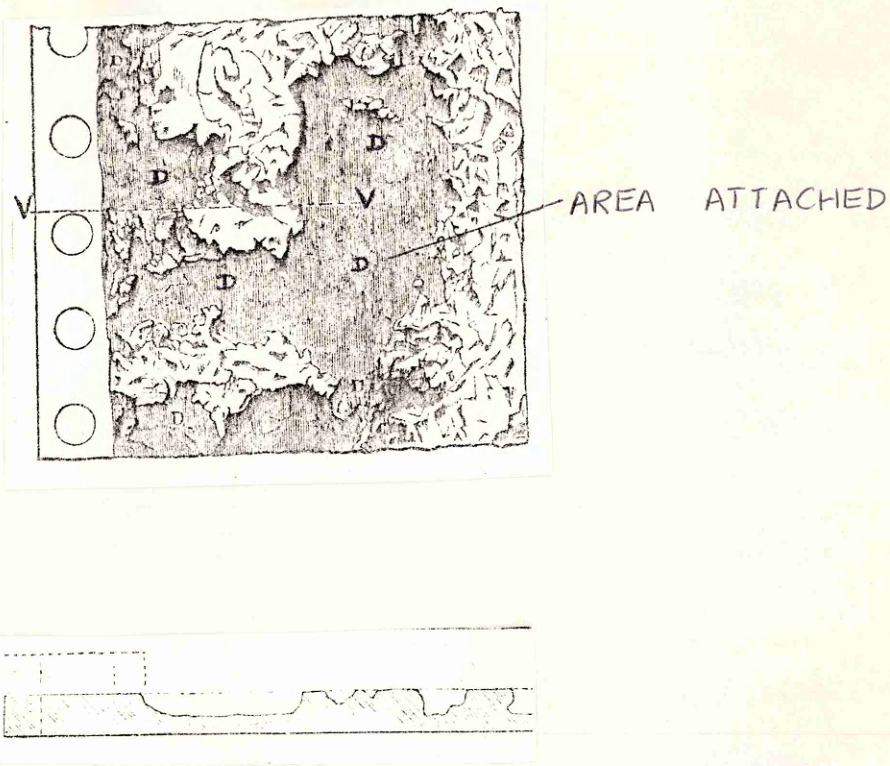


FIG. 23 THE SWEEP PLATE FROM OVER THE FIRE IN A PLAIN CYLINDRICAL BOILER[25]

Marten reported that he had observed internal corrosion where boilers had been fed with water from canals or streams in the neighbourhood of chemical works from which corrosive products had been discharged at intervals into the water. He stated:-(25)

"_ _ _ The corrosion takes place in isolated spots, but causes deep holes; which seems to be accounted for on the supposition that the scale previously upon the plate cracks during the cooling of the boiler for cleaning and forms a blister, so that a piece of about 2 inches is raised slightly from the iron. When the boiler is put to work, this blister becomes filled with the corrosive water, which is held there without circulation and causes corrosion. When the boiler is again emptied, these blisters may be seen, and if broken, show the blackened water and the injured surface. In future working each of these blisters forms a constant unprotected point for attack."

This observation by Marten of pit and blister formation is still upheld today.

Nearly all the information that was forthcoming on investigations into the effect of corrosion on boiler installations continued to come from engineers within the inspecting organisations. Consequently, the development of these institutions was strongly linked with the development in the understanding of corrosive action.

4.1.10. Waterline Corrosion

A typical multitubular marine boiler, used at this time is illustrated in fig. 24. the circulation taking place by the water ascending from the furnace crowns, the sides, backs and fronts of the combustion chambers and descending at the wings.

Hallet(125) observed that in this type of boiler, the water in the part below the level of the fire bars always contained the greatest percentage of solid matter and it was here that the greatest deterioration was expected to be found.

Double-ended boilers were subject to the same corrosive action as single-ended boilers but having a greater length, they were more prone to suffer from 'racking' strains, due to the difference of temperature between their upper and lower parts. One method of reducing this difference was to fit the internal feed pipe so that it led along on a level with the upper tubes. A method particularly useful in combatting corrosion was that of 'blowing down'.

The boilers were well washed out before filling and, after filling, a bucketful of soda was thrown through the top manhole cover. The steam was raised to about 30 lbs per sq. inch and a little blown out through the scum cocks. The scum pipe was fitted with a pan, as shown at S in fig. 24 and can be seen to have been like an inverted saucer. It was placed just above the level of the water for the scum to collect under it. This was blown off when steam was being raised.

Hallet reports from his experience that one of the most active causes of deterioration in boilers was the fact that when boilers were blown down, this was only done as far as the level of the bottom manholes, and they were then refilled, without care being taken to draw the water out of the bottom. He stated:-

"This process (of not properly draining) having been frequently repeated, the water at the bottom became so impregnated that the heads of the rivets and the lower half of the compensating rings round the manholes were corroded away, while the other parts of the boiler were in good condition."

Severe potential causes of corrosion were observed by engineers like Hallet, and devices, some of dubious value, were introduced to combat the corrosion. In many cases, the motive was sound but often the boiler operators were ignorant of both the operation and maintenance of any such devices.

Hallet[125] records the installation of 'hydro-kineters'. These were internal steam jet nozzles for stimulating the circulation of water in the cooler spaces below furnace flues. The principle behind this idea was

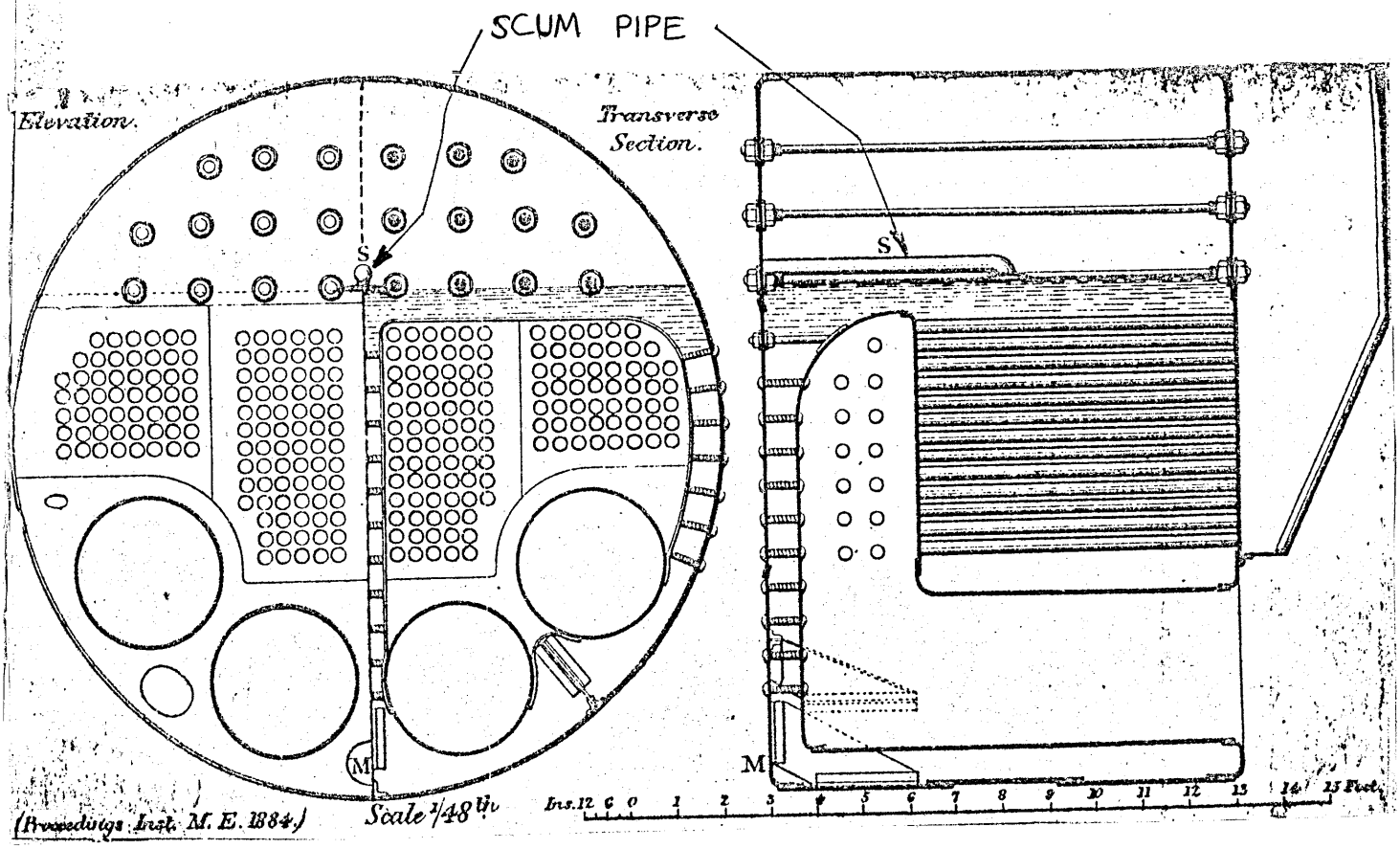


FIG. 24. ILLUSTRATING THE POSITION OF THE SCUM PIPE IN A MARINE BOILER.(123)

excellent, since corrosion is maximised under stagnant water conditions. However, he reported that the nozzles were never checked and became blocked.

Corrosion was also observed in the upper regions of boilers and was found to be particularly severe when there was an excess of oil, tallow and other greasy discharges from the engine. This was observed by Hallet[125] and also by Norris.[126] Norris also stated[127] that the decomposition of lubricants used for cylinders and slides produced fatty acids which dissolved the brass of the condenser tubes:-

"The resulting fatty acids, on passing into the boiler, converts the water into a solution of copper which acts 'chemico-galvanically' or electro-chemically upon the water and iron, causing corrosion."

However, the solution contained one in one million parts of copper, so this theory was not substantiated.

4.1.11. Global outlook

Explosions were also taking place in Germany.[128]

An explosion of two vertical cylinder boilers at Hüstan iron works tore one of the boilers in three pieces, one of which was completely rolled up. At the points of fracture, the iron was badly corroded and this was recorded as causing the explosion.

Another explosion of a Lancashire boiler at Zocherndorf colliery, resulted in the left flue tube being torn right across the top, at which place the iron had scaled off. The right flue-tube burst only partially at the top, and was crushed flat. The report stated that corrosion of the plates appeared to be the cause of the explosion.

Foolish behaviour by boiler owners does not appear to be confined to the British.

A report of an accident at Lindow Alcohol Distillery stated:-[128]

"_ _ _ Near the hole were four patches, which were covered with a dirty scale, evidently produced by a leakage of water through the patches. The water trickling through gradually caused the corrosion."

The attitude of some less responsible boiler owners was clearly the

same in both Britain[25] and Germany.[128]

Vogt[129] dealt with the effects of soluble substances contained in feed water and emphasised the necessity for material to be of uniform composition.

Diegel[130] found that the addition of phosphorus to zinc-bronze had been shown to improve its capacity for resisting the action of sea-water.

There was little impetus in Germany to carry out any detailed long term study of the problem. This was probably because of the lack of any well organised inspection and insurance organisation. The number of accidents appears to have been considerably less[128] and consequently public agitation was not as vocal.

Rinne[131] in a comprehensive article on boiler materials and corrosion referred to the numerous attempts that had been made to ascertain the exact causes of boiler corrosion in Germany. These followed along the same paths as in England. He described the problems of furrowing, wasting and pitting. He considered that the fault was often due to the metal of which the boiler was made. He considered that the open-hearth ingot metal which was used in boiler construction was in no way at fault. Like other investigators, he considered that air entering the feed water was an important factor. He thought that if proper feed-water was employed, free from air and carbon dioxide, and if the boiler was blown frequently enough, it would never show signs of corrosion.

A case of boiler-tube corrosion was reported from Amsterdam[132] in which tubes of a locomotive developed a serious leak, and it was found that small circular or elliptical holes had formed on the outside of the tubes. The analysis of the water was reported to disclose no peculiarities and no scale had been deposited. When the steel adjacent to the holes was polished, small crystals detached themselves from the outer surface, and microscopic examination revealed, in the corroded spots, the presence of comparatively large crystals and many fissures at right angles to the longitudinal axis of the tube, and these were initiation spots for corrosion cells. On

careful investigation, it was revealed that at the site of these holes, small drops of oil had accidentally dropped on the tubes.

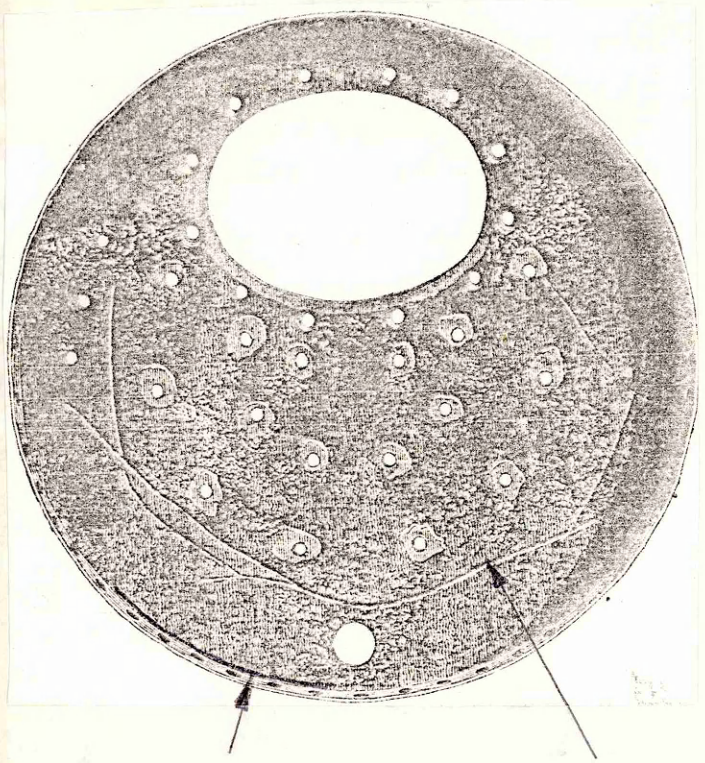
The Rail Road Gazette[133] illustrates an account from Paris, of the destructive corrosion of a steam-boiler which had been fed with rain-water collected from a zinc roof over a shop located in a district in which the atmosphere was heavily charged with acid vapours. Chemical analysis of the water showed it to contain a considerable percentage of sulphuric acid.

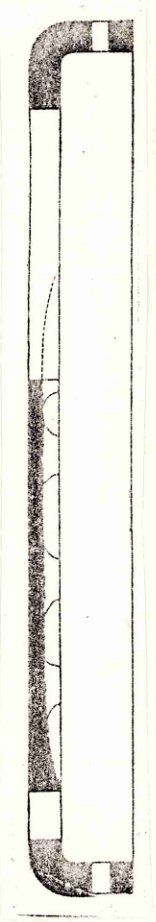
The corrosive action due to this rain water was very intense, especially at the rear end of the boiler. The plates and tubes began to pit badly, rivet-heads and submerged braces wasted away rapidly.

Fig. 25.[134] illustrates the boiler head at a coal mine in Western America. Water, impregnated with the products of the mine, was fed to the boilers; the severe corrosion resulting was credited to sulphur from the water. In some places, the corrosion was reported to be three fifths the thickness of the head, originally $^{5}/_{16}$ inch. The life of the boiler was eight months. Where the braces were attached, there was no corrosive action. The cause of the lines, which can be clearly seen on the diagram, was not explained. They are, however, a form of 'furrowing' and can be seen to take a contour equi-distant from the rim. However, this location is different from that normally sought by a furrow. Similar 'lines' were observed by Fremont and Osmond.[135]

Another reason assigned for the corrosion of boiler tubes, was the presence of hydrochloric acid, due to the decomposition of magnesium chloride in sea water at 212°F.[133]

Worthington[136] considered that this effect could be made minimal by reducing the amount of make-up feed from the sea as much as possible. He observed that naval boilers were not under steam on an average of more than one-third of their time, and no hydrochloric acid could be generated when the water was cold.





(134)

FIG. 25. A CORRODED BOILER HEAD.

A case was reported in Cassiers Mag.[137] of a steam boiler from one of the United States Naval Vessels after several months service on the Cuban blockade during the Spanish-American war. Some of the tubes were found to be entirely perforated and in one of the tubes corrosion had been so active, that 5 inches of the tube's length were entirely wasted and the free ends were worn down to paper thinness. The engineer was reported to be entirely unaware of this and had steamed into port at full steam pressure. The interesting fact was, that the spaces between the tubes were so solidly obstructed by scale, in the vicinity of the break, that no leakage had been noticed. Salt water had been used instead of fresh or distilled water and had caused this.

4.1.12. Fletchers influence on inspection techniques

A person who had a considerable influence on the drafting of boiler legislation, was Lavington E. Fletcher, who was the Chief Engineer of M.S.U.A. until his death in 1897.

The Memoirs[138] for the Institution of Mechanical Engineers, gave an indication of the very interesting life that he had led.

He had been engaged under I.K. Brunel as an assistant engineer and had erected bridges and tunnels all over the world. In 1861, he had been appointed Chief Engineer, under the then title of Chief Inspector, to the Association for the Prevention of Steam Boiler Explosions. In this capacity, he had been the instigator of many investigations into boiler explosions and in particular, had investigated and classified the different types of corrosion normal in these circumstances. Extracts from his reports to the M.S.U.A. formed a regular feature in the column of The Engineer during this period of his career. Like many engineers of this period, his earlier work had been within the scope of civil engineering, changing towards mechanical engineering as industry expanded.

It was only after the passing of these various Acts, (SEE refs. 139 - 146) that reliable statistics relating to boiler explosions first became

available to the public in general. Marten in 1866, had given a series of statistics, but he had not gone into any great detail, nor did he offer any comments on the figures he obtained.

Figs. 26 to 27 illustrate briefly a case study of a boiler explosion which occured at Blackburn in 1874, with a great loss of life.

Fig. 26 is a copy of the Telegram from the Chief Engineer of the M.S.U.A. about the explosion.

Fig. 27 shows the location of the fragments after the explosion, as produced on site from measurements taken by Fletcher.

Fig. 28 illustrates the back end of the boiler with the 'grooving' which had caused failure.

Figs. 29 and 30 are illustrations of interesting boiler explosions from M.S.U.A. archival materials, but the details are not known.

Royal Naval vessels were given exemption from inspection. This was probably due to mandatory requirements for secrecy in matters concerning a fighting force. These would be in direct opposition to the spirit of the Boiler Explosion Acts.

4.2. OTHER CASES

4.2.1. Railway bridges

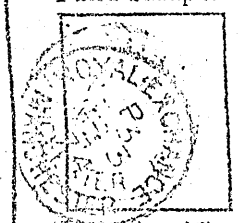
Apart from general observations, like those made by Siemens[19] Barnaby[111] and Bessemer,[114] on mild steel and iron used in boiler construction, general observations were made in the use of these materials for bridge building.

Matheson[20] remarked that he had seen "a beautifully made bridge" that had been put up twenty-five years earlier by Fox and Henderson and was placed over the Commercial Road at Stepney. The upper boom or box of the bridge had been riveted and caulked like a boiler, and was perfectly air-tight; the inside plates he observed were in perfect condition. Some of the parts exposed to the atmosphere had deep pits in all directions, materially weakening them. The worst part he found, was where the iron had been brought in contact with the wood. He considered the acid from the

Charges to pay £ .....

POST OFFICE TELEGRAPHS.

Dated Stamp of



Regulation as to Inland Telegrams.

If the Receiver of an Inland Message doubts its accuracy, he may have it repeated on paying half the cost of its transmission to him. In the event of an error having been made, the amount paid for repetition will be refunded on application to the Secretary.

Office of Origin Blackburn Handed in at 4-37 P.M. Sent out at 5 12 P.M.

From Fletcher Taylor & Co Ltd Chief Engineer Blackburn

To H. C. Fletcher Chief Engineer H.M. Explosives Inspectorate Leeds

Charge	
1/-	After explosion there fell pieces of roofing iron and coal and five children were killed. Please come and examine boiler as soon as possible
1/3	
1/6	
1/9	
2/-	

FIG. 26. TELEGRAM NOTIFYING I.E. FLETCHER OF BLACKBURN BOILER EXPLOSION. (Ack. Brit. Eng. Ins. Co. Ltd.)

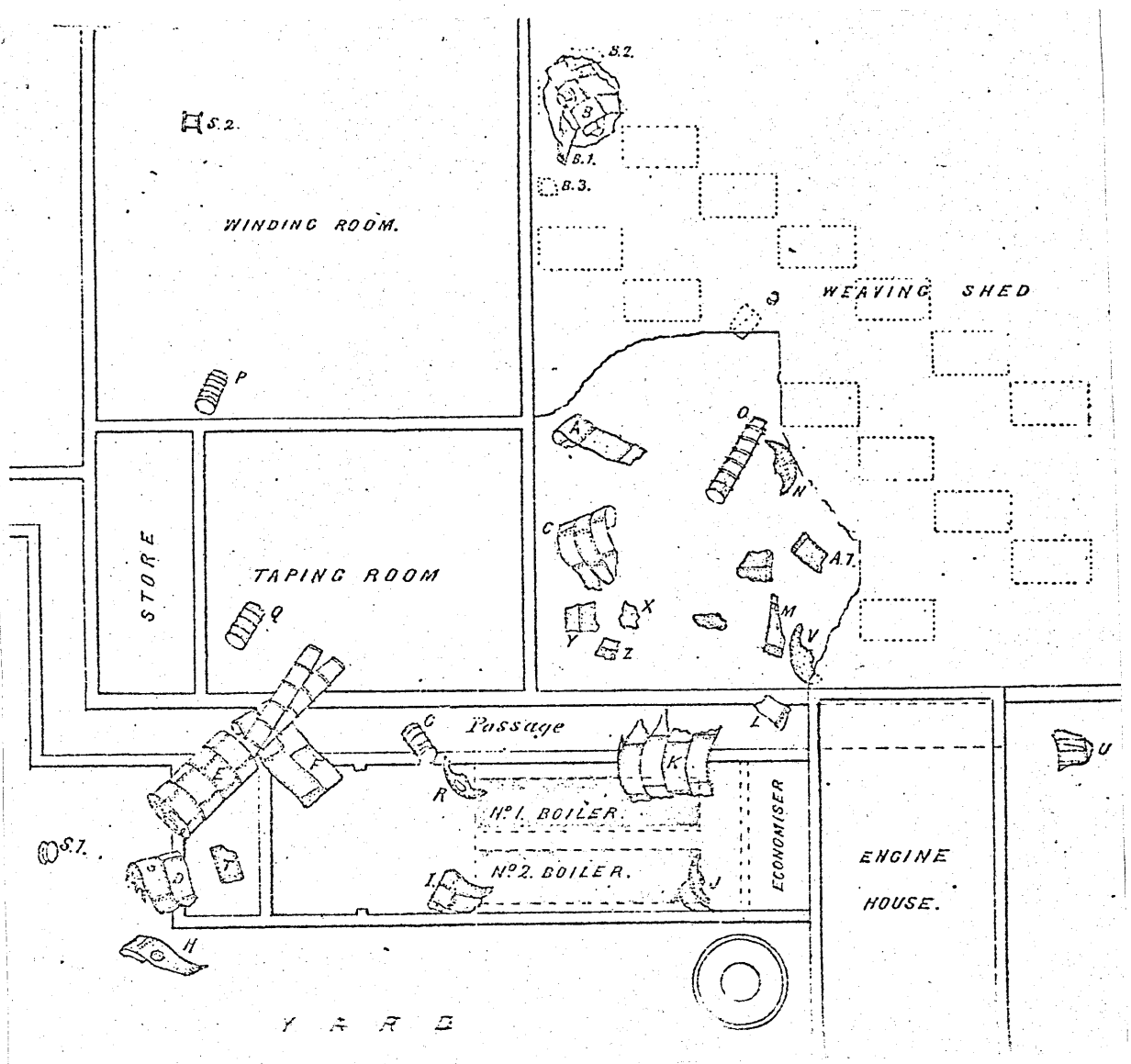


FIG. 27. LOCATION OF FRAGMENTS FOLLOWING THE 1874 BOILER EXPLOSION AT BLACKBURN. (Ack. Brit. Eng. Ins. Co. Ltd.)

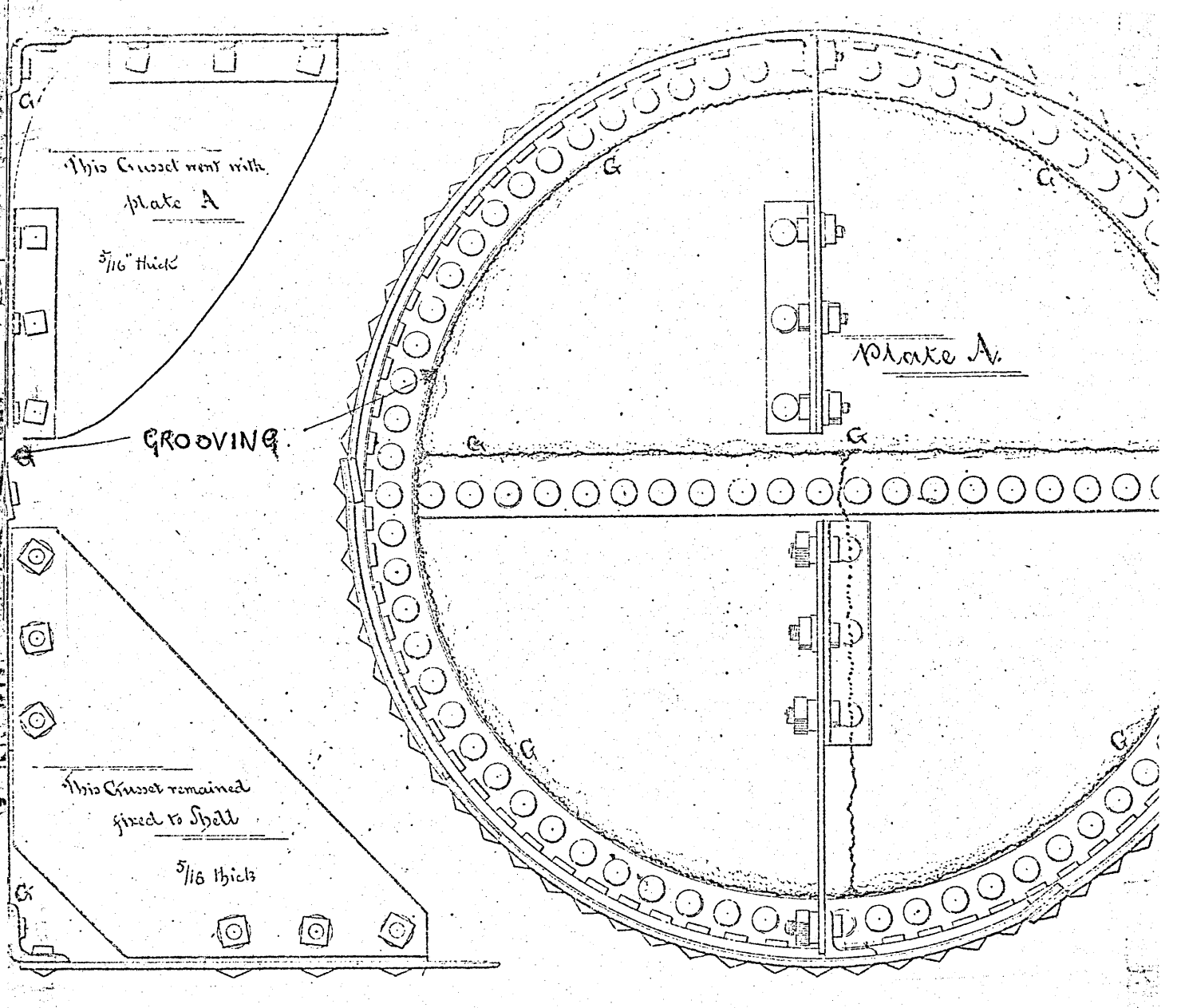


FIG. 28. DETAILS OF GROOVING WHICH CAUSED THE 1874 BLACKBURN EXPLOSION(A)

(Ack. Brit. Eng. Ins. Co. Ltd.)

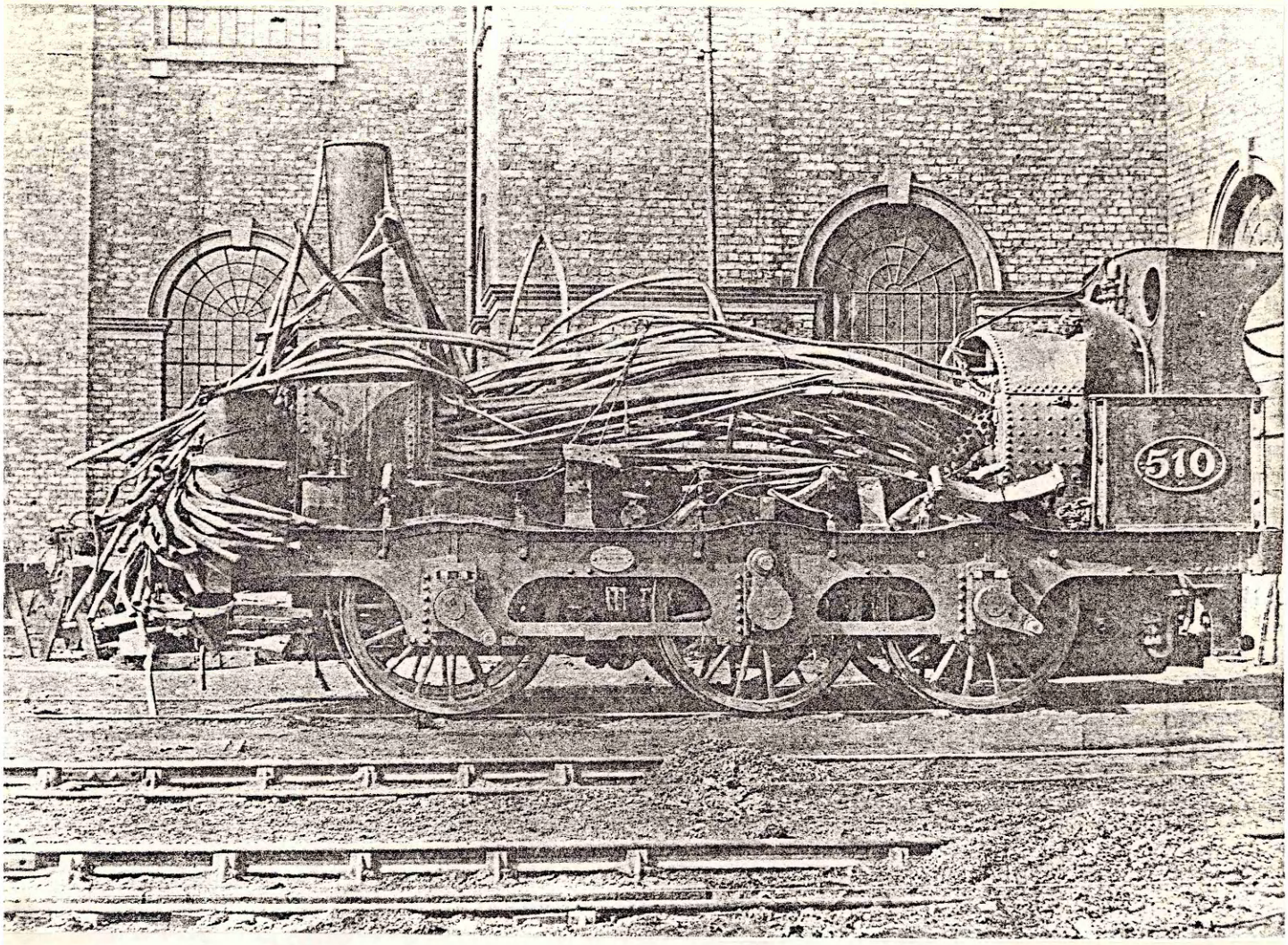


FIG. 29. LOCOMOTIVE BOILER EXPLOSION:- FROM M.S.U.A. ARCHIVAL MATERIAL. IT WAS A MID-NINETEENTH CENTURY NORTH EASTERN ENGINE IN THE SUPERINTENDENCY OF E. FLETCHER. (1854 - 83). (Ack. Brit. Eng. Ins. Co. Ltd.)

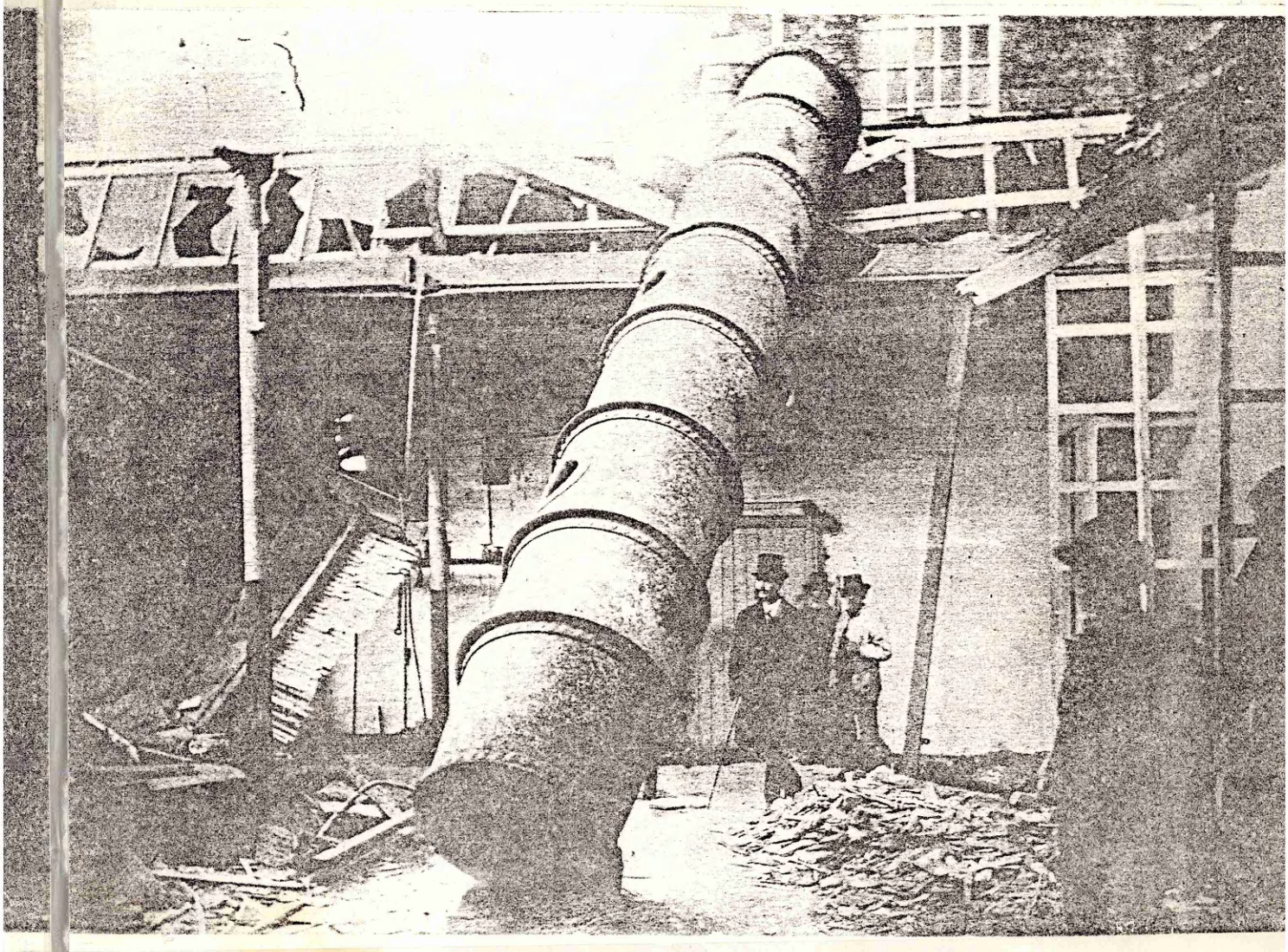


FIG. 30. FLETCHER MAKING A PRELIMINARY INSPECTION FOLLOWING AN EXPLOSION:-
DETAILS NOT KNOWN. (Ack. Brit. Eng. Ins. Co. Ltd.)

wood was the cause of the metal wasting from angle iron ½ inch thick down to a knife edge. In fact, this was probably a case of crevice corrosion.

He also remarked about another bridge that had been put up in 1860 and which was pulled down in 1880, in the centre of London. He observed that the rivet-heads were eaten away, and the Tee iron stiffeners were nearly all rusted away.

Matheson's remarks about the Commercial Road bridge prompted a retort from Cowper.[21] He observed that in bridges, which he had seen in the London area and which were made of laminated plates, rapid corrosion had taken place. He considered that protection should be adopted in making the riveted joints air-tight at the edges specifically excluding the damp air coming from the chimneys of locomotives.

An investigation[22] into the cause and failure of the Tay Bridge reported that where cast iron and wrought iron were connected by rivets in many parts of the structure they had corroded to such an extent, that failure resulted.

'Local galvanic circles' had formed at numerous points in the structure where the two metals were in contact and the corrosion so established was the cause of the disaster.

The tubular bridge over the St. Lawrence River, was also found to be in a similar condition and the result was the removal of the whole structure and the building of another bridge.

Further reports concerning the rapid corrosion of iron in railway bridges, was observed by Kent.[147] [148]

Rust, in some places up to one eighth of an inch in thickness, was extracted from a bridge on the Pennsylvania Railroad and sent to the laboratory of the Stevens' Institute for examination.

All the plates were observed to be covered on the other side with a thick coating of a sooty constituent, which was considered to have come from the smoke of the locomotives. Part of the rust was finely powdered,

put into a flask, and distilled water, free from ammonia, added. The flask was tightly corked, and exposed to a gentle heat for two weeks. The water was then filtered off. After careful analysis, it was deduced that the cause of the oxidation of the iron was due to the presence of carbonic, sulphuric and sulphurous acids. This was considered to be due mainly to the escaping gases from the locomotives.

Further observations on American bridges were made by Show.[149] He noticed a pair of lateral brace angles, crossing each other, one being completely rusted through, while the other one was only slightly 'specked'. The painting and all conditions of exposure and protection were exactly similar.

He found that the corrosion of this structural steel was influenced by its chemical composition. Manganese increased the corrosion while phosphorus retarded it.

4.2.2. Office Blocks

At the Annual Convention of the American Institute of Architects, in 1894, Post stated[23] that the iron beams removed by him from the old Times building, though in use for only thirty-five years, were rotten with rust. They had been enclosed in eight inches of brickwork. The iron came off in strips, clearly showing that rust had followed the lamination of the iron, the web being so rotten as to be easily broken by the finger.

This completely opposes views put by Matheson on protecting structures that[24]:-

"Iron built into lime or brickwork or masonary would remain for centuries almost in the same condition as when it was put in."

4.2.3. Propeller Blades

A practical example of the corrosion of steel in sea water was given from America, by King[150] in a paper on the corrosion of a cast steel propeller blade. The corrosion covered two-thirds of the back of the blade and occured soon after use. The working face at the front was in good

condition. Commenting on earlier steel blades imported from England in 1872, King stated that the engineers had said that[150] "they melted like sugar." The corrosion in these cases had been observed to be at the back of the blades at the front end, and holes five to seven inches diameter had been eaten through the blades in less than six months.

This corrosion, in fact, was probably caused by galvanic action between the propeller and hull of the ship.

4.2.4. Railway Lines

Apart from the consideration of iron and steel for bridges, another important application was that of railway lines. In this respect, Bell expressed[151] the opinion that "the cinder" in wrought iron rails would set up galvanic currents, and lead to more rapid corrosion.

The result of the experiments of the Admiralty Committees which were appointed to consider the causes of the deterioration of boilers, and which issued reports in 1877 and 1880, led to the conclusion that in all cases, wrought iron resisted corrosion better than steel. Where the conditions were not severe the differences observed were not great, but where the plates were daily dipped in water, and exposed, during the rest of the time, to the action of the atmosphere, the superiority of iron was very marked, while 'common iron' was less effected by corrosion than best Yorkshire iron.

4.2.5. Pipes and Components

Cast iron was one of the first materials to be investigated especially with its use as a constructional material in harbours. This was particularly important because of the loss of strength involved.[152]

A photograph appeared in Engineering[153] illustrating the unusual corrosion of an iron bar. The portion of the bar shown dark, being corroded. The bands of rust extended over both the ends of the bar, giving the appearance of being built up of layers of two different metals. This in fact could have been due to the lack of homogeneity in the material. (Fig. 32.)

In a paper dealing with the internal corrosion of cast iron pipes, Jamieson stated[107] that the interior of corroded pipes was generally in one of two conditions. When the iron was directly exposed to the action of the water, the rust was uniformly distributed, and grew rapidly. Where the iron had been protected by a coating of asphalt, the rust appeared in detached carbuncles or knots, where the protection was weakest, and gradually spread over the whole surface, ultimately growing as rapidly as when iron was unprotected. He considered that the corrosion appeared to be proportional to the volume of water passing through the pipe.

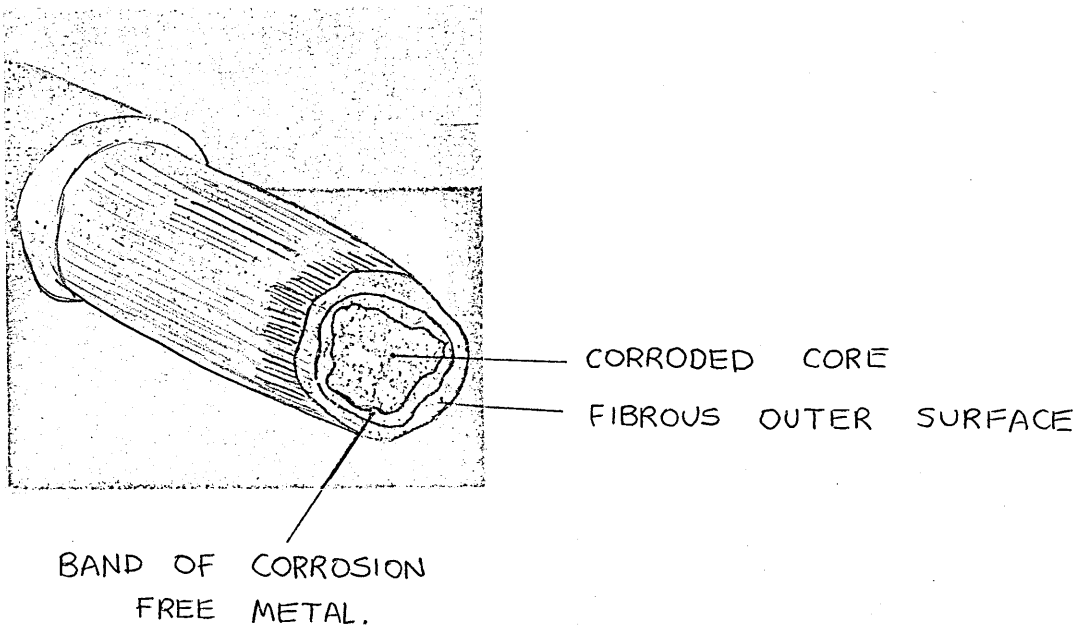


FIG. 32. BAND OF CORROSION FREE METAL, POSSIBLY DUE TO LACK OF HOMOGENEITY IN MATERIAL.(107)

CHAPTER 5

DETAILED SCIENTIFIC ANALYSIS

5.1. SCALE

The first specific examination of scale, was carried out by Mushet in 1840,[154] when he examined an iron heel post that had been in sea water.

The effect of scale was generally regarded to have a galvanic influence on iron with which it was in contact. Barnaby stated[155] that the action of oxide in this respect was as strong and continuous as that of copper. White, in 1881, observed[156] from experiments carried out at Portsmouth, that when black oxide was left on portions of steel plates, it produced pitting. John[157] described how, on examining small mounds of rust on the outside of a recently launched steel vessel, he found that under each heap of rust there was a small hole in the paint, not larger than the size of a pin's head and that beneath each hole, was embedded a small particle of black oxide in a pit in the plate.

The electrical aspects, already referred to, were studied by a number of different observers. Farquharson[158] described an experiment in which two plates, one of iron and one of steel, were carefully cleaned of scale, when it was found that they corroded practically alike, but on combining one plate, either of iron or steel, with the skin on, with another similar plate, from which the skin had been removed, it was found that the former did not corrode, while the latter corroded rapidly.

In 1882,[159] Andrews took eleven plates of wrought iron, which were bent over in a U shape, one half being covered with scale, and the other half polished bright, they were immersed in a cell with clean sea water, so as to make a battery, and the current produced, passed through a galvanometer. It was observed that the bright iron was positive to the scale, and a deflection of 17° was obtained on the galvanometer; this steadily decreased during the observations, until on the fourth day, it was only 0.75°

Lewes's[160] general comments fall in line with earlier experimenters. He took two clean plates of mild steel, separating their surfaces by a sheet of blotting-paper, moistened with sea water, and connecting them through a galvanometer, which then registered a deflection of 20°; on covering the surface of one plate with ferrous oxide, the deflection was only slightly increased to 25°; one of the surfaces with hydrated ferric oxide gave a deflection of 65°, while rust gave a deflection of 110° and magnetic oxide, the maximum deflection of the whole series, namely 112° so indicating the great galvanic activity of this oxide.

In spite of such apparently conclusive evidence, Phillips[161] in a paper read before the Institute of Marine Engineers, in 1890 gave reasons for believing that the scale of black oxide acted as a preservative of the iron and steel immediately underneath.

The reason for this discrepancy could be that, as the scale in Phillips' experiments was artificially prepared, it may have taken on the character of the Bower-Barff protective oxide.[50] Fortunately, Phillips supplied this experimental information and this emphasises the importance of this type of data being available.

The dual position of this oxide obviously caused some confusion judging by the remarks made before the Iron and Steel Institute by Head:-[162]

"I am afraid that the outside public will accuse this Institute of inconsistency. It has been said in this room only two days ago, that the great thing is to get rid of magnetic oxide from the surface of the iron used in ships and boilers. Now we are told that we should do our utmost to put magnetic oxide on to the iron _ _ _ ."

This was part of a discussion following a paper on the Bower-Barff protective oxide.

Liversidge in a paper read before the Australasian Association for the Advancement of Science, pointed out that although it was usually stated that iron rust consisted of the hydrated ferric oxide, he found on examining

a large number of specimens, that in almost every instance, the rust contained more or less magnetic oxide. This compared favourably with other observations.(163)

5.2. GALVANIC EFFECTS

Parker(115) considered that the relative size of the exposed and protected surfaces must have some influence on the galvanic currents, apart from whether scale was present or not. It can be seen from fig. 8 that these currents appear to be considerably effected by the different fluids to which the discs were exposed. It would appear that the discs in series D, which were exposed in the boiler containing zinc, had suffered more from galvanic action than the black discs in other boilers, while the samples immersed in the sea, suffered more than those exposed to the greasy water and moist air of the bilges. It can be seen that there was no practical difference between the loss of the black and of the bright discs exposed to the atmosphere, and it is unlikely that here at least, no galvanic action would take place.

One of the problems about making further deductions from Parker's work, is that there is no indication regarding the length of time the scale was present. Consequently, it is also impossible from the experimental method used by Parker for a rate to have been determined at which the black oxide might have been acting galvanically upon the neighbouring bare patches.

These unanswered questions, probably prompted Andrews to investigate further the influence of galvanic currents in wrought iron and steel plates in sea water.(164) In this work, he continued the trend of relaying more information about experimental procedure. Although Mallet(16)(17)(18) had carried out an exhaustive series of experiments and classified his results, he gave little indication of his method of approach to testing. Little mention was made of the conditions under which the experiments were carried out and of any surface preparation prior to testing. From the period of this

work, experimenters began gradually to reveal more information as the importance of scientific testing and correlation began to be realised. They appreciated more that if the results that they produced were to be meaningful and be suitable for evaluation by other scientists, then these data would need to be supplied. From around 1840 to 1880 a detection can be made of a gradual change of emphasis from a general philosophising about the problems of corrosion to that of supplying detailed scientific facts about how the information was produced. Diagrams of the testing equipment, methods of holding the specimens, even the full details of the screws used for attachment were given by 1884.

At this time, 1885, the controversy between the relative corrosion resistance of wrought iron and steel had still not abated. In that year Andrews published results of a series of experiments comparing these two metals connected together and immersed in sea water.

Polished plates were dried at 212°F and weighed. A bright plate of each of the metals was connected by a brass screw clip and copper wire 0.105 inches in diameter, with a plate of bright wroughtiron of the same size at distances of five-eighths of an inch apart in each case. This arrangement was then immersed in a wooden trough, and the sea water changed each month during the period of the investigation. Andrews stated that he endeavoured to maintain a good contact between the metals throughout. At the periods stated, in fig. 33a, each pair of plates was carefully attached to a galvanometer for a day. Andrews then determined the "electrochemical position of the metals and the electromotive force."(164)

At the end of the periods given, the plates were removed, washed and polished with leather, dried at 212°F and weighed. The results are given in fig. 33.

They were then connected again and re-immersed in the sea water for further observations.

The whole of the plates, where then taken out of the water and after long exposure, were found to be completely covered with:-

Description.	Combined Carbon.	Loss per Square foot of Surface.							Electromotive Force in Volts and Electro-Chemical positions of the Metals during First and Second Periods.[1]		
		Corrosion during 4 weeks.	First period. Corrosion during 56 weeks.		Second period. Corrosion during 51 weeks.		Total period. Corrosion during 110 weeks.		42 weeks from commencement.	52 weeks from commencement.	101 weeks from commencement.
		Bright steel, &c., plates in galvanic circuit with plates of the same metal but covered with scale (Magnetic Oxide).	Division 1. Bright steel, &c., plates in galvanic circuit with wrought-iron plates	Division 2. Wrought-iron plate connected with the various steel, &c., plates.	Division 1. Bright steel, &c., plates in galvanic circuit with wrought-iron plates.	Division 2. Wrought-iron plate connected with the various steel, &c., plates.	Division 1. Bright steel, &c., plates in galvanic circuit with wrought-iron plates.	Division 2. Wrought-iron plate connected with the various steel, &c., plates.			
	Per cent.	Grains.	Grains.	Grains.	Grains.	Grains.	Grains.	Grains.			
Wrought iron No. 1	trace	31·12	..	..	..	..	..	..	..	..	..
Wrought iron No. 2 (Wortley Best scrap)	none	..	..	..	..	..	..	..	..	..	..
Soft Bessemer steel	0·150	28·00	196·80	147·54	329·06	256·39	525·86	403·93	0·001 P	0 0004 P	0·002 N
Soft Siemens-Martin steel	0·170	27·20	200·71	133·81	326·70	219·91	527·41	353·72	0·0004 N	0·002 N	0·006 N
Soft cast steel	0·460	26·56	203·08	136·98	332·75	265·40	535·83	402·38	0·0004 P	0·001 N	0·0001 N
Hard Bessemer steel	0·510	44·16	184·60	154·34	352·25	263·41	536·94	417·75	0·0004 P	No E.M.F.	E.M.F. very feeble (Steel N)
Hard Siemens-Martin steel	0·720	35·84	146·88	150 57	316·43	268·43	463·31	419·00	0·004 N	No E.M.F.	0·0004 P
Cast metal No. 1	2·010	36 56	226·63	105·08	303·14	232·39	529·77	337·47	0·004 P	0·009 P	0·002 N
" No 2	0·670	..	178·78	139·50	271·75	245·69	450·53	385·19	0·001 N	0·003 P	0·001 P

FIG. 33 CORROSION OF WROUGHT IRON, STEEL AND CAST METAL PLATES IN SEA-WATER IN 'GALVANIC CONNECTION'. (164)

"soft slimy oxides of iron"[164]

which were found to be easily removable, the upper half of each plate presenting a characteristic reddish colour of rust.

The results in fig. 33 illustrate the considerable tendency to corrosion of the steels in relation to wrought iron. The advantage in favour of the iron as compared with the steels amounting roughly to 25 per cent, for the period of two years and ten weeks. These results confirm in many respects, the work of Parker[115] published a few years earlier. Andrews[5] published a further series of results in 1887, on the relative electro-chemical positions of wrought iron, steels and cast metal in sea water and other solutions.

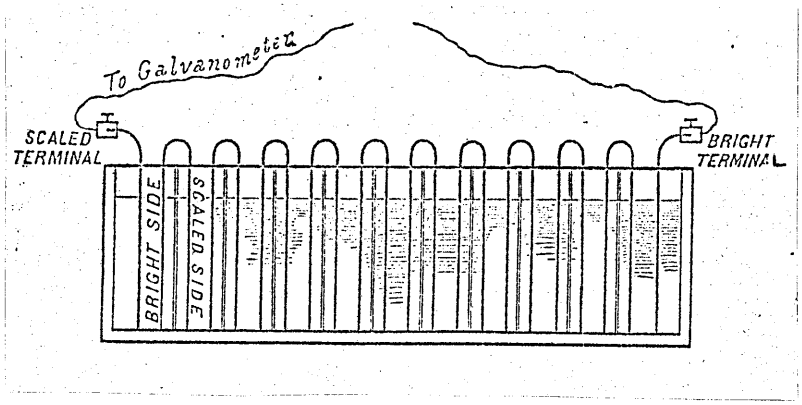
Eleven plates of wrought iron were each bent double, half of each plate was polished bright and the other half left covered with scale, just as it left the rolls; they were then placed in a clean porous cell, (Daniell's battery,) filled with sea water. (fig. 33a.)

They were all arranged in a voltaic series as illustrated in the diagram and attached to the terminals of a galvanometer. The results he obtained however, were not significantly different from these other experiments carried out under similar circumstances.

Andrews continued these further investigations of 1887[165] but nothing of any great significance resulted.

The pattern was similar to his earlier experiments, which is useful, since valid comparisons are possible.

The preparation of the materials was similar but the specimens were placed one half of an inch apart, and immersed in sea water in an arrangement of cells forming a voltaic series of cells. (fig. 35.) A constant supply of sea water was maintained during the experiment, the water being changed monthly, as before. The results he obtained are given in fig. 34. In this first group, plates of steel covered with scale and bright plates of the same steel were used.



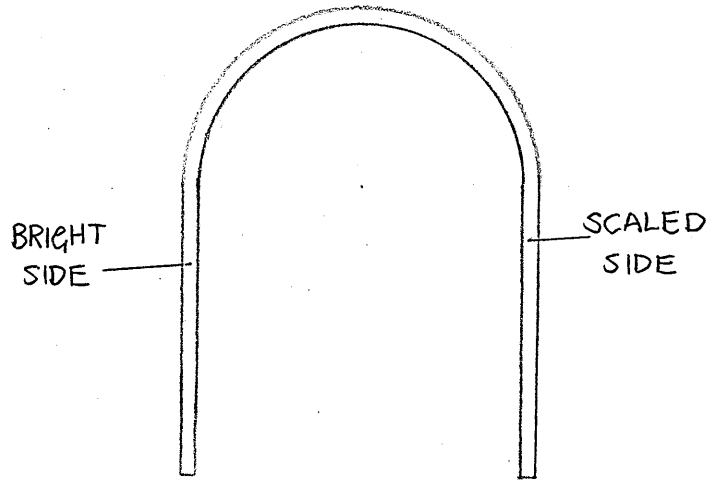


FIG. 33a ANDREWS' EXPERIMENTAL ARRANGEMENT(164)

Description.	Combined Carbon.	Set 1. Period 1. Column 1. Loss per square foot of surface of bright steel, &c., plates after exposure in Sea-water for 16 weeks to E.M.F. in column 3.	Set 1. Period 1. Column 2. Time from commencement of experiment.	Set 1. Period 1. Column 3. E.M.F. in Volt.	Set 1. Period 2. Column 1. Loss per square foot of surface of bright steel, &c., plates after exposure in Sea-water for 52 weeks to E.M.F. in column 3.	Set 1. Period 2. Column 2. Time from commencement of experiment.	Set 1. Period 2. Column 3. E.M.F. in Volt.	Set 1. Total period. Loss per square foot of surface of bright steel, &c., plates after exposure in Sea-water for 68 weeks to E.M.F. stated.	Set 2. Period 1. Column 1. Loss per square footofsurface of the steel, &c., plates exposed in Sea-water for 16 weeks to E.M.F. in col. 3.	Set 2. Period 1. Column 2. Time from commencement of experiment.	Set 2. Period 1. Column 3. E.M.F. in Volt.	Set 2. Period 2. Column 1. Loss per square footofsurface of the steel, &c., plates exposed in Sea-water for 52 weeks to E.M.F. in col. 3.	Set 2. Period 2. Column 2. Time from commencement of experiment.	Set 2. Period 2. Column 3. E.M.F. in Volt.	Set 2. Total period. Loss per square footofsurface of the steel, &c., plates exposed in Sea-water for 68 weeks to E.M.F. stated.	Set 3. Column 1. Loss per square foot of surface of the plates exposed in Sea-water to E.M.F. in column 2 for 16 weeks.	Set 3. Column 2. Average E.M.F. to which the metals were exposed for 16 weeks.
	Per cent.	Grains.	Hour.	0·227	Grains.	Days.	0·054	Grains.	Grains.	Hour.	0·849	Grains.	Days.		Grains.	Grains.	During about first half of period about 1·17 volt. During about second half of period about 0·86 volts.
Wrought iron No. 1	trace	113·84	1	0·149	364·58	45	0·028	478·42	243·68	1	0·434	517·07	114	0·091	760·75	1324·88	
„ No. 2			2	0·168		144	0·028			2	0·247		147	0·101			
(Wortley Best scrap)	none		2½	0·186	394·19	151	0·037			3	0·191	534·94	151	0·091			
			24	0·186		155	0·046			24	0·130		155	0·072			
			Days.							Days.							
Soft Bessemer steel	0·150	127·20	37	0·072	337·26	159	0·028	464·46	221·28	2	0·168	382·82	177	0·037	604·10	1351·04	
			68	0·054		208	0·019			3	0·149		235	0·016			
Soft Siemens-Martin steel	0·170	157·36	88	0·037	208·39	239	0·028	365·75	159·28	4	0·149	497·72	238	0·072	657·00	1343·92	
			91	0·028		242	0·019			5	0·149		244	0·072			
Soft cast steel	0·460	173·76	108	0·019	405·34	248	0·028	579·10	234·56	6	0·130	552·66	255	0·081	787·22	1396·32	
			112	0·019		259	0·019			7	0·111		272	0·072			
Hard Bessemer steel	0·510	129·28		Average E.M.F. 0·038 Volt.	409·40	275	0·019	538·68	238·80	15	0·130	524·60	275	0·072	763·40	1079·28	
						312	0·034			16	0·072		297	0·154			
Hard Siemens Martin steel	0·720	164·56			377·65	316	0·043	542·21	252·32	18	0·072	523·35	300	0·128	775·67	1385·28	
						329	0·028			46	0·081		308	0·165			
Hard cast steel	1·407					347	0·022		261·84	53	0·081		312	0·149		1602·00	
						367	0·023			60	0·081		364	0·119			
Cast metal No. 1	2·010	184·88			351·00		Average E.M.F. 0·030 Volt.	539·78	263·60	63	0·081	570·68		Average E.M.F. 0·095 Volt.	834·28		
										96	0·111						
										112	0·054						
										Average E.M.F. 0·093 Volt.							

FIG. 34 RESULTS OBTAINED (164)

In the second group, bright steel and wrought iron were prepared and arranged as before.

In the final group, bright steel plates were arranged in connection with bright wrought iron.

This voltaic series of plates was then connected to a battery for sixteen weeks. Two batteries in fact were used alternately. . . In these experiments during the first part of the time, the direction of the current was arranged so that the iron plates formed the anode metal. The direction of the current was reversed during the latter part, the steel plates then constituting the anode metals. This alternation in the direction of the current was made to approximate in an intensified way, the effects which could be produced on structures by the interchanges of electro-chemical positions between the metals that Andrews had observed earlier.(164)

In Fig. 34 are set out the results of these groups of experiments.

Sets 1 and 2 show the relative greater corrosion induced by the increased galvanic action to which the metals were exposed. Set 3 shows the relatively greater corrosion induced by the largely increased galvanic action to which the metals were exposed for the shorter period of time stated.

The first set shows for period 1, that an exposure to an average electromotive force of about 0.038 volts in sea water for sixteen weeks produced less corrosion in the wrought iron 'No. 1.' than in any of the steels. A more prolonged exposure of fifty two weeks to a similar average force of about 0.03 volts, set 1 period 2, appeared to reverse this result in favour of the steels, with the exception of the soft cast steel and hard Bessemer.

Examining set 2, period 1:-

In the case of galvanic action between copper and wrought iron, the wrought iron under these conditions corroded more than most of the steels,

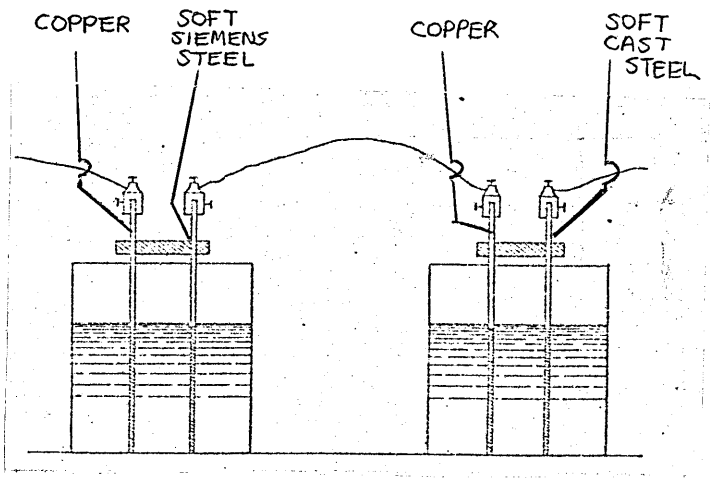


FIG. 35. VOLTAIC SERIES OF CELLS USED BY ANDREWS'[166]

during sixteen weeks exposure to an average electromotive force of about 0.093 volts; during the second period of fifty-two weeks, the loss in all the metals considerably increased, and in the case of the 'soft' cast steel exceeded that of the iron.

However, when the metals were under the action of a much higher electromotive force (3.6 volts) as in set 3, the wrought iron had the advantage over all the steels, with the exception of 'hard' Bessemer, from which it would appear that wrought iron is corroded less in sea water by large electromotive forces than steels.

It must however, be appreciated that these experiments of Andrews' subjected the materials to conditions far more intensive than would normally occur and consequently they are mainly of academic interest.

Among the facts brought out by these experiments which may not have been appreciated widely at the time, is the importance of guarding against accidental galvanic action in structures. Andrews carried out a similar series of experiments investigating the action of tidal streams on metals.(166)

Galvanic action was also considered to be a contributory factor in the corrosion of boilers and bridges.(167)

Cresson did not give any detailed reasons, but observed that galvanic forces were an accelerator of oxidation. He stated:-

"Many steam boilers have come under my observation in which the corrosion was slight and effected all parts equally, others in which the metal of a single sheet only was attacked, the corrosion of which sheet protected the remainder of the boiler almost as efficiently as if the sheet had been replaced by one of zinc.

"The most striking instance of the effect of introducing a sheet of metal of greatly differing electro-condition that occurs to me is that of a boiler which had been in use for a considerable length of time without showing any unusual tendency to corrosion, when from some cause it became necessary to replace a sheet by a new one. The result of the introduction

of a new sheet was to set up at once a strong galvanic action by which every sheet in the boiler was corroded except the new one. Samples of iron cut from the edges of the old and from the new sheets were placed in a bath to which a few drops of dilute acid were added and a connection made with a galvanometer, resulting in the production of a new current; the purer iron corroding, and protecting that which contained the greatest amount of carbon.

"The injurious effect consequent upon the junction of masses of wrought iron of varying electro-chemical properties, is therefore increased when steel is joined to wrought iron, as is frequently the case in locomotive boilers in the tubes and tube sheets.

"The necessity for the selection of iron with reference to its electric condition, applies equally to the material employed for bridges or any structure which is to be built-up from separate sheets and bars of iron.

"Determinations of the compositions of the metal or of the percentage of carbon in it by chemical analysis are unnecessary; an ordinary workman furnished with a coarse galvanometer and a weak acid bath can ascertain the exact electro-condition of each sheet or bar more rapidly than he can examine the quality by the ordinary tests of bending on an anvil, hot or cold. With the metal of bridges, vessels and especially steam boilers, the deterioration by corrosion is more to be feared than is mechanical wear."

Cresson in this work approached the problems more from a philosophical standpoint than scientific. He was by profession a medical doctor and although many of these suggestions he makes would not have been practical, he emphasised the major problem areas. In doing this, he was able to focus important factors for future investigation by scientists or engineers who would be capable of carrying out a detailed analysis.

5.3. MAGNETIC EFFECTS

Apart from his contribution to knowledge on the effect of galvanic

forces acting on iron and steel structures, Cresson was probably the first to make comments on the effect of magnetising iron on corrosion rate.

His comments were sparse, but these in themselves made in 1875, probably triggered off ideas in the mind of Andrews, who between 1885 and 1892, carried out a series of experiments to investigate this effect.

Andrews, by 1887,[168] had already made a significant contribution to the knowledge of corrosion science and at this time, decided to investigate the effect of magnetisation on the relative electrochemical position of a pair of bright iron bars, one magnetised by a coil, the other not magnetised, when simultaneously exposed in circuit to the action of various powerful oxidising agents and saline solutions.

For this investigation, he used numerous specially prepared long polished rods of soft wrought scrap iron 0.26 inch diameter. Two pieces were adjacently cut from a long finely polished iron rod, so that the pieces might, as nearly as practicable, be of identical chemical composition. They were firmly held in a wooden supporting frame and immersed to an equal depth in a solution contained in a U-tube which was also ridgidly supported. The U-tube, was then immersed in four pints of cold water to ensure equal temperature conditions during experimentation, for the respective solutions in each limb. The cold water was maintained in steady circulation around the tubes. The rods were connected in circuit with a galvanometer, which was under constant telescopic observation. A removable coil of copper wire mounted on a large bobbin 6 inches long, enclosed one of the U-tube limbs, the coil surrounding the upper portion of the long bar requiring magnetisation. A single cell bichromate battery, easily put in or out of operation was attached to the coil, and the battery was recharged with the same strength of solution for each observation. After a short time, during which, steady galvanic equilibrium had been established between the two iron rods, the coil was put into operation. The rod designated 'A' was magnetised, and in most solutions became positive to the other rod. Andrews observed that this was due to the increased action of the acid or saline solution on the iron rod. This was under magnetic

influence because it became surrounded by a slightly stronger saline solution than the other unmagnetised rod 'B', which was apparently from his observations, less acted upon.

In some cases, (fig. 36. columns 4,5,7,8,) there appeared to be a maximum point reached and after the more violent action of the acid had expended itself, a reduction of the e.m.f. between the rods was generally reached as the solution in the B-tube gradually approached an equilibrium of composition compared with the solution in the limb A of the tube. The solutions that Andrews used are given in fig. 36.

The results from these experiments were sufficiently encouraging to Andrews for him to undertake a further series of experiments with different reagents using the same equipment and similar specimens.(169)

Again, for every set of experiments one of the steel bars was magnetised, the other being retained in its unmagnetised state. The results compared favourably with his earlier set of experiments and from these combined results, Andrews considered that the explanation of this magneto-chemical phenomenon was possibly connected with local currents he found developed in the magnetised bar between the more highly and less magnetised parts when the rod was immersed in suitable solutions. He made further observations and noted that when a magnetised bar is immersed, a local galvanic current is set up between the polar terminals and the less magnetised portion of the bar, which is the centre part. He found the more magnetically neutral zones acting electro-negatively in relation to the poles. Under these conditions, the magnetised bar formed the other element in the same solution.

Probably, the main conclusion of this work could be that he showed that a current flows from a magnetised bar towards an unmagnetised one, when the two are immersed in suitable solutions, The result was dependent both on the nature and strength of the solution, and also on the extent of the magnetisation of the metal. It was also demonstrated that when a

Time from commencement and duration of magnetisation in minutes.		E.M.F. in volt, and electrochemical position of magnetised bar compared with the unmagnetised bar, the positive or negative position of the former being respectively indicated by the signs + and −.				
		Column 4.	Column 5.		Column 6.	
		Potassium bi-chromate and nitric acid.	Ferric chloride and nitric acid.		Nitric acid, sp. gr. 1·388, one part, and three parts water.	
		II.	I.	II.	I.	II.
hrs.	mins.					
0	0	0·000	0·000	0·000	0·000	0·000
0	1	..	..	−0·004	+0·026	+0·004
0	2	+0·009	..	+0·002	..	..
0	2½	+0·005	..	+0·002	+0·020	+0·005
0	3	+0·009	..	+0·011	+0·020	+0·007
0	4	+0·010	..	+0·013	+0·016	+0·009
0	5	+0·007	..	+0·013	+0·014	+0·009
0	6	..	..	+0·020	..	..
0	7	..	..	+0·016	..	..
0	7½	..	..	+0·006	+0·011	+0·011
0	8	..	..	+0·022	..	..
0	9	..	..	+0·034	..	+0·011
0	10	+0·006	..	+0·011	+0·008	+0·011
0	11	..	..	+0·014	..	..
0	12	..	..	+0·011	..	..
0	12½	+0·009	..	..	..	+0·010
0	13	..	..	+0·009	..	..
0	14	..	..	..	..	..
0	15	+0·004	..	+0·003	+0·009	+0·005
0	16	..	..	..	..	..
0	17	..	..	..	..	..
0	17½	..	..	+0·009	..	..
0	19	..	..	..	..	..
0	20	+0·007	+0·009	+0·007	+0·007	+0·005
0	22½	..	..	..	..	..
0	25	+0·005	+0·018	+0·004	+0·001	+0·003
0	30	+0·003	+0·013	+0·003	+0·001	+0·004
0	35	+0·001	+0·013	+0·002	+0·011	+0·003
0	40	+0·004	+0·023	+0·003	+0·012	+0·004
0	45	+0·001	+0·009	..	+0·013	+0·003
0	50	+0·002	+0·004	..	+0·009	+0·006
0	55	..	+0·005	..	+0·019	+0·007
1	0	+0·008	+0·003	+0·001	+0·013	+0·007
1	5	..	..	..	..	..
1	15	..	..	..	..	..
1	30	..	..	..	..	..
1	45	..	..	..	..	..
2	0	..	+0·007	..	..	..
2	20	..	..	..	..	..
3	0	..	..	..	..	..
3	15	..	..	..	..	..

Time from commencement and duration of magnetisation in minutes.		E.M.F. in volt, and electrochemical position of magnetised bar compared with the unmagnetised bar, the positive or negative position of the former being respectively indicated by the signs + and −.					
		Column 7.		Column 8.	Column 9.	Column 10.	
		Nitric Acid, sp. gr. 1·388, 1 part, and 4 parts water.		Aqua regia, 2 parts HNO_3 and 1 part HCl, diluted to one-half with water.	Hydrochloric acid, sp. gr. 1·16, diluted to one-half with water.	Sulphuric acid (concentrated), sp. gr. 1·84.	
		I.	II.	II.	II.	I.	II.
hrs.	mins.						
0	0	0·000	0·000	0·000	0·000	0·000	0·000
0	1	..	+0·004	+0·002	..	..	..
0	2½	..	+0·006	..	..	..	−0·001
0	3	..	+0·009	..	..	..	..
0	4	..	+0·012	..	..	..	..
0	5	+0·012	+0·011	+0·004	−0·0004	−0·003	−0·002
0	6	..	+0·010	..	..	..	..
0	7½	..	+0·007	+0·006	..	..	..
0	9	..	..	..	..	..	..
0	10	+0·011	+0·003	+0·011	−0·001	−0·004	−0·003
0	11	..	+0·005	..	..	..	..
0	12	..	+0·005	+0·013	..	..	..
0	12½	..	..	..	..	..	..
0	13	..	+0·005	..	..	..	..
0	14	..	+0·003	+0·014	..	..	..
0	15	+0·013	+0·001	+0·027	−0·001	−0·005	−0·005
0	16	..	..	+0·027	..	..	..
0	17	..	..	+0·014	..	..	..
0	19	..	..	..	..	..	..
0	20	+0·014	+0·004	+0·025	−0·001	−0·005	−0·005
0	22½	..	..	+0·019	−0·001	..	..
0	25	+0·013	+0·004	..	−0·001	−0·005	−0·006
0	30	+0·012	+0·005	+0·004	−0·001	−0·007	−0·005
0	35	+0·013	+0·005	..	−0·001	−0·003	−0·008
0	40	+0·012	+0·004	..	−0·001	−0·009	−0·006
0	45	+0·012	+0·003	+0·001	−0·001	−0·011	−0·005
0	50	+0·012	+0·003	..	−0·001	−0·012	−0·005
0	55	+0·012	+0·004	+0·001	−0·002	−0·014	−0·006
1	0	+0·011	+0·004	+0·001	−0·003	−0·018	−0·006
1	15	..	..	..	−0·003	−0·022	−0·007
1	30	..	..	..	−0·002	−0·023	−0·009
1	45	..	..	..	−0·004	..	−0·008
2	0	..	..	..	−0·004	..	−0·009
2	20	..	..	..	..	..	−0·028
3	0	..	..	..	..	..	−0·009
3	15	..	..	..	..	..	−0·021

FIG. 35. EFFECT OF MAGNETISATION (168)

magnetised rod constituted one element in a suitable electrolyte, local currents flowed from the more highly magnetised polar terminals towards the less magnetised or neutral parts. These conditions would cause the magnetised rod to be more generally acted upon by the electrolyte, the composition of the solution surrounding it being also effected.

The apparent tendency of the N. pole to become electropositive in an electrolyte caused Andrews to undertake further research to try and determine a reason for this.(170)

He supposed that the bars would be equally magnetised permanently, then when the magnet bars were placed in the upright position, the magnetism induced in the bars by the earths magnetic force would in one magnet strengthen, and in the other oppose the permanent magnetism, so the stronger pole would be the North one at the bottom.

To investigate this, he arranged a wooden stand, the thick upper cross-bar of which was hollow and formed a tank sufficiently large to hold the required electrolyte. The ends of the two magnetised steel bars were securely inserted from below through two holes in the base, so that only the upper terminal discs to the magnets were exposed to the solution. The holes were accurately drilled so that when the bars were forced in, the arrangement was fluid-tight and care was taken so that only the terminal plates of the magnets were exposed to the action of the solution. The steel rods were connected with a galvanometer which was introduced into the circuit, and the electrolyte was then poured in the upper receptacle and the readings of the galvanometer noted. He used a new wooden stand for each experiment and new steel magnets employed for each observation. In many experiments the electrolyte was first introduced to the lower ends of the bars, and observations first taken of the relative electrochemical positions of the N and S terminals at the lower ends of the magnets. The solution was afterwards removed, the lower bar ends cleaned and the electrolyte subsequently placed in the upper receptacle. By this means, an indication of the relative electro-chemical position of both the upper and lower polar discs

of the same pair of steel magnets was afforded. The results of these experiments are recorded in fig. 37. sets 1 to 1V and fig. 38 sets V & V1.

An examination of the results of the total observations, on the steel magnets, in fig. 38 in which the electrolyte (cupric choride solution) was placed below the magnets, gave an average e.m.f. of 0.014 volts, whereas the observations made with the electrolyte above the magnets yielded an average e.m.f. of 0.011 volts. The results tended to indicate that the 'positivity' of the upper N polar terminal was reduced relatively to some extent when the electrolyte was placed above the magnets.

In the final series of experiments that Andrews carried out and published in 1892[171] he again investigated the influence of magnetisation on the corrosion of steel.

This work, although not as complex as his previous investigations, was probably by far the most useful.

He selected as the corrosive fluid, a solution of cupric chloride. He used steel bars, the lengths and diameters of which are given in fig 39. As before, each pair was cut adjacently from a long finely polished rod, so that the bars were as near as practicable alike in general composition and structure. For every set of experiments, one of the steel bars was magnetised, the other being retained in its unmagnetised state. The bars were each weighed and immersed in an equal quantity of cupric chloride solution, in separate beakers, a considerable distance apart. After the completion of the periods of immersion, stated in fig. 39, each bar was taken out, and on removal from the solution the electro deposited copper was drawn off from the remains of the steel bar. The rods were then carefully washed and cleaned, dried and then weighed. This was repeated for each experiment.

Twenty-nine experiments were carried out and the results indicate that the corrosion rate of the steel due to magnetic influences was about 3 per cent.

Observing the results in fig. 39, the extent of the loss by corrosion may be attributed probably to the variation in the extent to which the bars

Electro-chemical effect between north and south polar terminals of magnetised steel bars. E.M.F. in volt. The electro-chemical position of the north polar terminal was positive, except where otherwise indicated.

Time from commencement of experiment.	Cupric chloride solution.			
	Set I. Average of 10 experiments.		Set II. Average of 10 experiments.	
	Electrolyte below.	Electrolyte above.	Electrolyte below.	Electrolyte above.
seconds.				
0	0·010	−0·018	−0·011	−0·007
30	0·004	0·011	0·001	0·001
minutes.				
1	0·007	0·000	0·006	0·005
2	0·004	0·004	0·008	0·007
3	0·010	0·004	0·014	0·012
4	0·016	0·009	0·021	0·014
5	0·011	0·014	0·018	0·018
6	0·016	0·011	0·016	0·021
7	0·017	0·015	0·016	0·026
8	0·020	0·012	0·013	0·027
9	0·021	0·014	0·013	0·026
10	0·014	0·020	0·015	0·024
11	0·025	0·014	0·017	0·022
12	0·021	0·025	0·016	0·021
13	0·046	0·011	0·019	0·018
14	0·023	0·012	0·019	0·017
15	0·025	0·020	0·021	0·015
16				
17	0·033	0·011	0·021	0·015
18				
19				
20	0·024	0·018	0·023	0·015
21				
22				
23				
24				
25	0·025	0·014	0·022	0·015
26				
27				
28				
29				
30	0·025	0·013	0·023	0·017
35	0·026		0·031	0·009
40	0·036			
45	0·022			

Electro-chemical effect between north and south polar terminals of magnetised steel bars. E.M.F. in volt. The electro-chemical position of the north polar terminal was positive, except where otherwise indicated.

Time from commencement of experiment.	Cupric chloride solution.			
	Set III. Average of 10 experiments.		Set IV. Average of 8 experiments.	
	Electrolyte below.	Electrolyte above.	Electrolyte below.	Electrolyte above.
seconds.				
0	−0·002	0·001	0·010	−0·022
30	0·006	0·009	0·003	0·005
minutes.				
1	0·003	0·005	0·004	0·002
2	0·003	0·005	0·005	0·005
3	0·007	0·007	0·006	0·011
4	0·011	0·009	0·006	0·012
5	0·013	0·009	0·009	0·009
6	0·016	0·008	0·010	0·009
7	0·018	0·007	0·008	0·007
8	0·016	0·008	0·010	0·012
9	0·016	0·008	0·012	0·008
10	0·016	0·010	0·011	0·007
11	0·015	0·008	0·013	0·002
12	0·013	0·008	0·012	0·008
13	0·015	0·010	0·013	0·005
14	0·016	0·015	0·015	0·009
15	0·016	0·015	0·014	0·007
16	0·018	0·013		
17	0·019	0·018	0·010	0·006
18	0·019	0·014		
19	0·014	0·013		
20	0·013	0·015	0·013	0·009
21	0·017	0·014		
22	0·013	0·013	0·020	0·004
23	0·014	0·013		
24	0·013	0·012		
25	0·011	0·012	0·007	0·003
26				
27	0·017	0·014		
28				
29				
30	0·013	0·011	0·007	0·011
35				0·018
40				0·021
45				0·018

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FIG. 37. EFFECT OF MAGNETISATION FURTHER RESULTS (A)

Electro-chemical effect between north and south polar terminals of magnetised steel bars. E.M.F. in volt. The electro-chemical position of the north polar terminal was positive, except where otherwise indicated.

Time from commencement of experiment.	Cupric sulphate solution.			
	Set V.		Set VI.	
	Electrolyte below.	Electrolyte above.	Electrolyte below.	Electrolyte above.
seconds.				
0	0·009	−0·014	−0·011	0·004
30	0·005	−0·006	−0·004	0·005
minutes.				
1	0·006	0·000	−0·003	
2	0·007	0·004	0·000	
3	0·006	0·003	0·000	0·000
4	0·006	0·002	0·002	0·002
5	0·007	0·003	0·004	0·002
6	0·009	0·009	0·006	0·003
7	0·010	0·009	0·010	0·002
8	0·010	0·006	0·016	0·000
9	0·010	0·004	0·020	
10	0·010	0·003	0·023	
11	0·012	0·002	0·023	
12	0·013	0·000	0·023	0·004
13	0·016		0·025	0·009
14	0·020	0·000	0·028	0·010
15	0·041	0·000	0·030	0·011
16	0·054		0·030	0·011
17	0·110		0·027	0·009
18	0·122		0·018	0·009
19	0·054		0·016	0·014
20	0·023		0·016	0·015
21	0·011		0·014	0·016
22	0·009	0·000	0·027	0·014
23	0·000	0·009	0·041	0·018
24	0·004	0·010	0·016	0·038
25	0·004	0·010		0·030
26		0·011		0·014
27		0·014		0·004
28		0·018		0·009
29		0·025		0·009
30		0·038		0·010
31		0·054		
32		0·072		
33		0·110		
34		0·203		
35		0·226		
hours.				
2		0·006		

Electro-chemical effect between north and south polar terminals of magnetised steel bars. E.M.F. in volt. The electro-chemical position of the north polar terminal was positive, except where otherwise indicated.

Time from commencement of experiment.	Cupric bromide solution.			
	Experiment No. 71.	Experiment No. 73.	Experiment No. 75.	Experiment No. 79.
	Electrolyte below.	Electrolyte below.	Electrolyte below.	Electrolyte below.
seconds.				
0	0·009	0·006	−0·009	−0·004
30	0·004	0·010	−0·004	0·006
minutes.				
1		0·007	−0·001	0·006
2		0·006	0·003	0·007
3	0·000	0·011	0·004	0·006
4	0·002	0·014	0·002	0·006
5	0·005	0·014	0·004	0·009
6	0·007	0·020	0·003	0·009
7	0·009	0·024	0·003	0·007
8	0·009	0·025	0·003	0·007
9	0·006	0·027	0·004	0·006
10	0·007	0·025	0·005	0·005
11	0·007	0·028	0·003	0·004
12	0·009	0·028	0·009	0·003
13	0·009	0·032	0·010	0·002
14	0·010	0·036	0·011	0·001
15	0·011	0·038	0·010	0·001
16		0·040	0·011	0·002
17	0·014	0·040	0·009	0·003
18		0·044	0·009	0·003
19		0·044	0·006	0·004
20	0·016	0·043	0·009	0·004
21		0·043	0·006	0·005
22	0·020	0·048	0·004	0·006
23		0·041	0·003	0·005
24		0·041	0·003	0·003
25	0·019	0·041	0·005	0·003
26		0·041	0·005	0·004
27		0·040	0·002	0·006
28		0·040	0·004	0·003
29		0·041	0·004	0·003
30	0·015	0·041	0·006	0·005

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FIG. 38. EFFECT OF MAGNETISATION FURTHER RESULTS (B)

Size of bars.		Time of exposure in cupric chloride solution.		Quantity of cupric chloride solution.	Loss in weight of unmagnetised steel bar.	Loss in weight of magnetised steel bar.	Increased loss in weight of the magnetised steel bar.
Length.	Diameter.						
in.	in.	h.	m.		grains.	grains.	per cent.
4½	0·296	19	30	10 fluid ozs.	247·00	260·00	5·27
3	0·296	24	0	10 „	153·00	167·40	9·41
3	0·296	24	0	10 „	179·30	191·30	6·69
3	0·296	24	0	10 „	241·30	247·90	2·73
3	0·296	24	0	10 „	247·60	253·60	2·42
3	0·260	12	0	10 „	96·70	98·94	2·32
3	0·296	12	0	10 „	112·01	122·85	8·80
3	0·296	24	0	4000 fluid grs.	196·08	212·60	8·43
3	0·296	24	0	4000 „	179·80	187·34	4·19
3	0·296	24	0	4000 „	206·38	206·85	0·23
3	0·296	24	0	4000 „	189·03	190·54	0·80
4	0·250	24	0	10 fluid ozs.	233·43	237·30	1·70
4	0·250	24	0	10 „	221·26	227·46	2·80
4	0·250	24	0	10 „	219·53	223·14	1·19
4	0·250	24	0	10 „	229·40	230·22	0·36
4	0·260	24	0	10 „	224·13	228·72	2·05
4½	0·301	24	0	10 „	236·74	237·19	0·19
4½	0·301	15	35	10 „	215·32	219·59	1·98
4	0·260	18	30	10 „	210·54	215·30	2·26
4½	0·301	15	0	10 „	203·64	208·06	2·17
4	0·260	14	15	10 „	187·37	187·99	0·33
4½	0·301	6	0	4200 fluid grs.	165·04	173·10	4·88
4½	0·301	6	30	4200 „	164·17	171·99	4·76
4½	0·301	6	3	4200 „	164·92	169·39	2·68
4½	0·301	6	0	4200 „	151·13	152·24	0·73
4½	0·301	6	0	4200 „	211·50	221·37	4·67
4½	0·301	13	45	4200 „	259·53	262·21	1·03
4	0·260	13	0	4200 „	216·62	217·08	0·21

AVERAGE LOSS 3·05%

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FIG. 39 EFFECT OF MAGNETISM FURTHER RESULTS (C)

were magnetised. The results indicate that magnetisation exerts an effect though small, on the extent of the corrosive action of copper salts on iron and steel. This is possibly owing to local currents set up by magnetisation between the polar and central portions of the bars, inducing greater chemical action.

Andrews in fact, was the only scientist to publish any substantial work on the influence of magnetism on the corrosion of metals. Although this has its obvious disadvantages, since his results cannot be compared with other work his experimental technique throughout was consistent and this gives validity to the comments expressed.

5.4. STRESS EFFECTS

Apart from his extended activity with magnetism effects, Andrews interest in corrosion activity by 1892, was to be extended into the field of stress-corrosion.(172) Although many scientists had investigated the effect of forces on materials, Andrews was probably the first to examine the effect of stress on the corrosion of metals. This is a significant paper, not only because it was the first to be published on the subject, but also because of the importance of stress-corrosion in the twentieth century.

The metals used were large rolled wrought iron bars and wrought iron hammered shafts, a variety of Bessemer and Siemens' steel forged shafts and alloy steels.

The various metals were prepared in the form of bars $3\frac{1}{8}$ and $3\frac{1}{4}$ inches in diameter, and some were forged shafts $4\frac{1}{8}$ inches and up to $5\frac{1}{2}$ inches in diameter. The plates were $^{5}/_{32}$ inch thick machined to dimensions given in Fig. 40. In the whole of the experiments the metals were perfectly bright. The observations Andrews divided under three headings:- Experiments on the influence of (1) tensile stress on corrosion, (2) torsional stress on the corrosion of metals in sea-water, (3) flexion stress on corrosion.

For the first set of experiments, from a bar of each of the metals under investigation, the centre section was machined down to $\frac{3}{4}$ inch. They were then stressed to produce an elongation of 20 per cent between gauge points 3 inches apart.

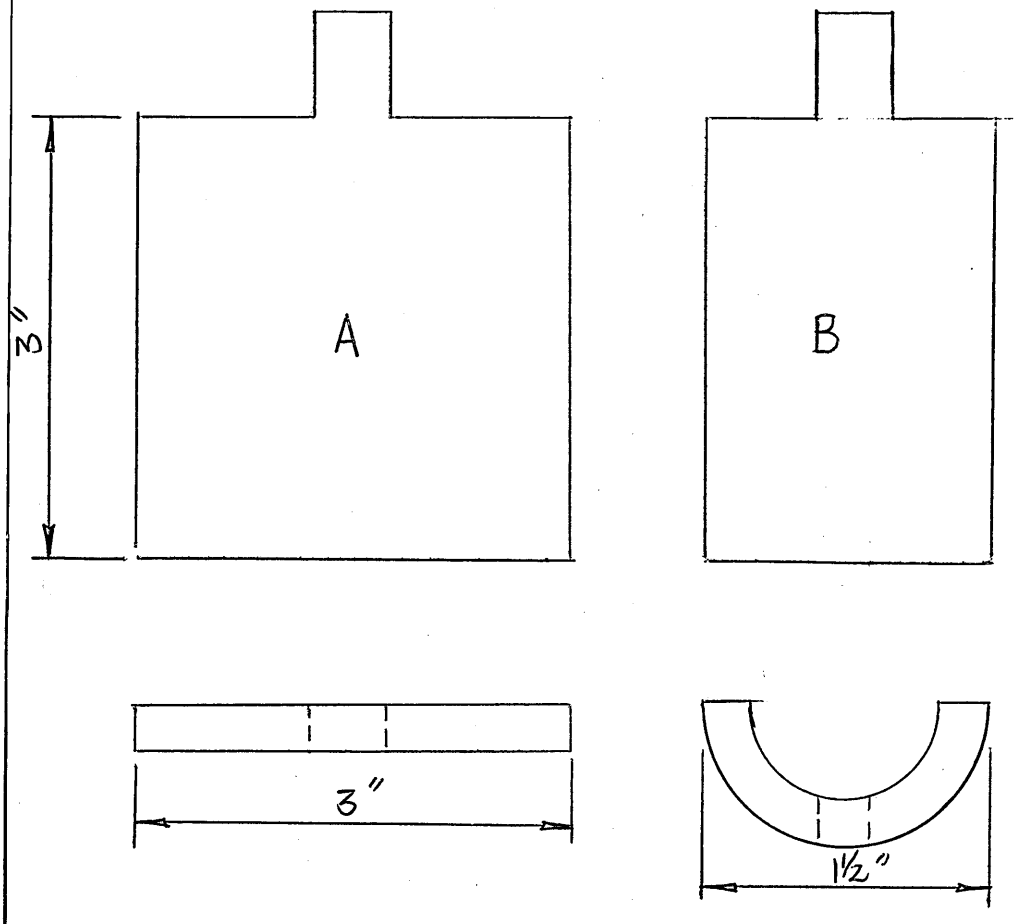
Details of the respective strains are given in fig. 41. After having been strained, the piece was cut in two at the centre C, Fig. 42. and the two halves were turned to the dimensions shown by the shaded portion. The 'strained' end A, was left untouched in the lathe, up to the point where there was any reduction in the diameter caused by the tensile stress, just as it came from the testing machine, and the 'unstrained' end B of the other half was turned exactly to the dimensions of piece A, fig. 42. Thus, both halves of the same piece of metal were reduced to the same size, the tapered end A, being the portion which had been strained to the extent stated in fig. 41.

The other tapered end B, consisted of unstrained metal, or at least of metal which had been considerably less under the influence of stress than A.

The two halves, A and B, were then immersed as a galvanic couple in a saturated solution of sodium chloride, and in some of the experiments on the influence of torsional stress on corrosion in sea water as an electrolyte.

Galvanic contact between the two pieces of metal was made only momentarily at the time of reading the galvanometer, and the difference of potential between the 'strained' and the 'unstrained' metals thus observed. The terminals of the bars were connected to a galvanometer placed in circuit, and the deflections of the galvanometer were recorded in the tables. The e.m.f. recorded in the observations was known from the current value of the galvanometer deflections in conjunction with the ascertained resistances in the circuit. In each case, it afforded an approximate measurement of the relative corrosibility of the 'strained' and 'unstrained' sections of the metal. The observations that Andrews found are given in figs 43 a & b and 44a.

A current was observed between the two bars, and the unstrained bar was found to be in the electropositive position (similar to zinc in a galvanic couple).



(172)

FIG. 40. DIMENSIONS OF PLATES USED TO EXAMINE FLEXIONAL STRESS ON CORROSION

Description of Metal.	Tensile Stress applied to the Metals previous to the Corrosion Experiments of Set I, Tables IV, V, VI.					Remarks.
	Original Dimensions, Diameter in Inches.	Distance between Datum Points in Inches.	Applied Stress per Square Inch in Tons.	Elongation per cent.	Reduction of Area per cent.	
Wrought-iron, Sets 1, 2, 3, 4 (hammered shafts)	1·000	10	20·50	20·7	32·7	Specimen broken.
Wrought-iron, Set 5 (hammered shaft)	1·000	8	21·64	19·0	22·5	„ „
Bessemer steel, Set 1 (hammered shaft)	0·798	8	40·44	24·7	37·6	„ „
Bessemer steel, Set 2 (hammered shaft)	0·798	8	37·80	26·7	47·2	„ „
Siemens steel, Set 1 (hammered shaft)	0·798	8	43·89	16·5	39·6	„ „
Siemens steel, Set 2 (hammered shaft)	0·798	8	43·70	20·0	31·6	„ „
Large bars: Soft Siemens steel	0·875	8	26·11	20·0	18·5	„ unbroken.
Hard „ „	0·875	8	59·07	14·0	48·4	„ broken.
Soft Bessemer steel	0·875	8	25·32	29·0	19·5	„ unbroken.
Hard „ „	0·875	8	45·54	20·0	32·3	„ broken.
Soft cast-steel	0·875	8	32·43	20·0	21·1	„ unbroken.
Hard „ „	0·872	8	43·75	2·7	2·2	„ broken.
Silicon steel	0·875	8	24·24	20·0	21·1	„ unbroken.
Aluminium steel	0·875	8	32·91	20·0	22·5	„ „
Nickel steel	0·875	8	37·14	20·0	22·5	„ „
Copper steel	0·875	8	35·72	20·0	20·5	„ broken.
Chromium steel	0·875	8	45·69	none	none	„ broke suddenly.
Wrought-iron	0·750	8	23·76	20·3	17·9	Specimen unbroken.

FIG. 41. RESULTS OF THE APPLICATION OF TENSILE STRESS (172)

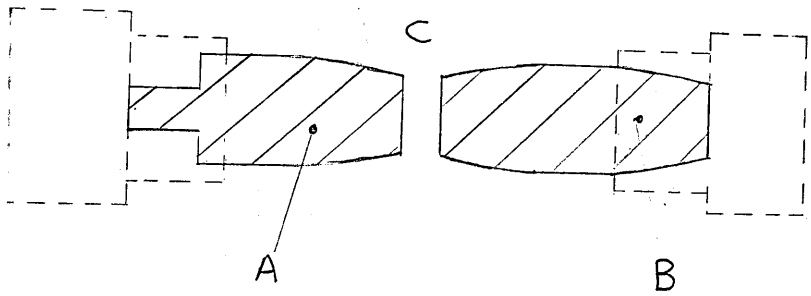


FIG 42 SPECIMEN USED FOR STRESS EXPERIMENTS(172)

Time from Commencement of Experiment.		Electro-chemical position of the unstrained metal, Positive, except where otherwise specified. Electromotive Force in Volt.								
		Wrought-Iron Forged Shafts.					Bessemer Steel Forged Shafts.		Siemens Steel Forged Shafts.	
		Set 1.	Set 2.	Set 3.	Set 4.	Set 5.	Set 1.	Set 2.	Set 1.	Set 2.
	0	0·002	0·020	0·034	0·038	0·009	0·022	0·013	0·011	0·025
Seconds	30	0·002	0·025	0·034	0·038	0·009	0·024	0·017	0·010	0·023
Minute	1	0·003	0·028	0·036	0·038	0·009	0·023	0·019	0·009	0·020
Hours	1	0·011	0·031	0·030	0·020	0·005	0·011	0·008	0·002	0·002
,,	6	0·004	0·043	0·009	0·011	0·003	0·005	0·004	0·002	0·003
,,	18	0·003	0·010	0·007	0·008	0·003	0·005	0·005	0·002	0·003
Days	1	0·003	0·009	0·006	0·007	0·002	0·006	0·005	0·002	0·002
,,	2	0·002	0·005	0·007	0·006	0·003	0·006	0·005	0·003	0·002
,,	3	0·006	0·005	0·006	0·005	0·003	0·006	0·005	0·002	
,,	4	0·009	0·004	0·009	0·004	0·003	0·006	0·004		
,,	6	0·007	0·003	0·010	0·007	..	0·006	0·004		
,,	7	0·009	0·003	..	0·009	..	0·006	0·004		
AVERAGE		0·006	0·027		0·004		0·010		0·009	
			0·027	0·019		0·011		0·004		

(a)

Time from Commencement of Experiment.		Electro-chemical position of the unstrained metal, Positive, except where otherwise specified. Electromotive Force in Volt.					
		Soft Siemens Steel.	Hard Siemens Steel.	Soft Bessemer Steel.	Hard Bessemer Steel.	Soft Cast-Steel.	Hard Cast-Steel.
	0	0·013	0·010	0·009	0·009	0·009	0·001
Seconds	30	0·014	0·011	0·009	0·009	0·007	0·002
Minute	1	0·014	0·011	0·010	0·009	0·007	0·002
Hours	1	0·006	0·004	0·054	0·004	0·001	0·0004
,,	6	0·002	0·002	0·011	0·004	0·003	0·0004
,,	18	0·001	0·001	0·004	0·004	..	0·0004
Days	1	0·001	0·001	0·004	0·004	0·002	0·001
,,	2	0·0004	0·001	0·004	0·003	0·001	0·001
,,	3	0·001	0·002	0·004	0·003	0·002	
,,	4	0·001	0·001	0·004	0·001	0·001	
,,	6	0·002	0·001	0·005			
,,	7	0·002	0·001	0·004	..	0·001	
AVERAGE		0·005		0·019		0·003	
			0·005		0·006		0·001

(b)

FIG. 43. TENSILE STRESS EXPERIMENTS (a) FORGED SHAFTS (b) LARGE BARS(172)

This indicated that the 'unstrained' metal was being more rapidly acted upon by the solution, and was so being corroded more rapidly than the 'strained' metal.

With similar specimens, the 'strained' metal 'A' was immersed in a saturated solution of sodium chloride, in connection as a galvanic couple with a polished copper rod of the same dimensions, and the pair were attached to a delicate galvanometer of known constants. The extent of the e.m.f. was determined and results recorded. (fig. 44(b).)

The 'unstrained' metal was placed in galvanic connection with a polished copper rod, of the same dimensions and from the same rod as that used with bar A. The steel in the couple yielding the greatest current was shown to be most acted upon by the electrolyte and from the results it can be seen that in these experiments the 'unstrained' metals corroded most under these conditions of experimentation. fig. 44(b).

In the second set of experiments, the influence of torsional stress on the corrosion of metals in sea water was investigated.

A similar range of materials was used and from each material, a portion was machined out from a shaft or forging to the dimensions given in fig. 45.

The pieces were then subject to a torsional strain sufficient to twist the part B ¼ inch in diameter, to an angle of 180°. After this operation the whole piece was cut in half at point C, and the unstrained part A, was turned to the dimensions of the strained part B. The two portions were then immersed in sea water. Connection was made with the galvanometer as in the other experiments, the direction of the current observed indicating relative corrosibility of the 'strained' and the 'unstrained' metal. At the conclusion of the experiment, the parts B and A of each metal were machined down and their inside properties examined. (Figs. 46 and 47.)

In every instance the 'unstrained' metal was the electro-positive element and hence was being corroded from the action of the sea water more than the strained metal.

Time from Commencement of Experiment.	Electro-chemical position of the unstrained metal, Positive, except where otherwise specified. Electromotive Force in Volt.					
	Silicon Steel.	Aluminium Steel.	Nickel Steel.	Copper Steel.	Chromium Steel.	Wrought-Iron.
0	0·004	0·009	0·005	0·014	0·003	0·001
Seconds 30	0·005	0·006	0·006	0·014	0·003	0·002
Minute 1	0·009	0·006	0·007	0·014	0·002	0·004
Hours 1	0·003	0·003	0·003	0·002	0·001	0·001
„ 6	0·0004	0·002	0·001	0·002	0·001	0·001
„ 18	..	0·001	0·001	0·002	0·001	0·001
Days 1	0·001	0·002	0·001	0·002	0·000	0·001
„ 2	0·004	0·004	0·002	0·003	0·001	0·001
„ 3	0·002	0·003	0·004	0·004	0·001	0·001
„ 4	0·002	0·004	0·003	0·006		
„ 6	..	0·002	0·002	0·007		
„ 7	..	0·001	0·001			
AVERAGE	0·004	0·004	0·003	0·006	0·001	0·002

(a.)

Time from Commencement of Experiment.	Electro-chemical position of the unstrained metal, Positive, except where otherwise specified.					
	Series A. Unstrained Cast-Steel with Copper Rod.	Series B. Strained Cast Steel with Copper Rod.	Increased Electromotive Force Indicating the Increased Corrosion of the Unstrained Bar.	Series A. Unstrained Aluminium Steel with Copper Rod.	Series B. Strained Aluminium Steel with Copper Rod.	Increased Electromotive Force Indicating the Increased Corrosion of the Unstrained Bar.
0	0·158	0·122	0·036	0·122	0·105	0·017
Seconds 30	0·146	0·113	0·033	0·127	0·110	0·017
Minutes 1	0·136	0·110	0·026	0·122	0·105	0·017
„ 5	0·101	0·097	0·004	0·110	0·077	0·033
„ 10	..	..	..	0·072	0·061	0·011
AVERAGE			0·023			0·022

(b.)

FIG. 44. TENSILE STRESS EXPERIMENTS (a) LARGE BARS (b) SMALL BARS COLD DRAWN (172)

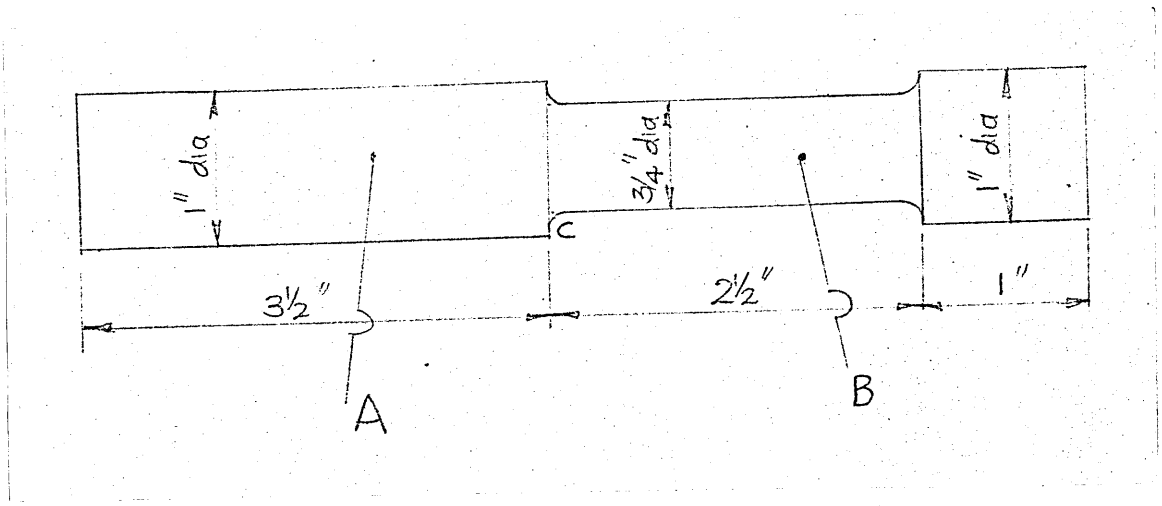


FIG 45 MODIFIED SPECIMEN USED DURING TORSION EXPERIMENTS(172)

Time from Commencement of Experiment.	Electro-chemical position of the unstrained metal, Positive, except where otherwise specified. Electromotive Force in Volt.						
	Description of Metals.						
	Wrought-Iron, Rolled Bar.	Wrought-Iron, Hammered Shaft.	Siemens Steel, Hammered Shaft.	Siemens Steel, Hammered Shaft.	Bessemer Steel, Hammered Shaft.	Soft Siemens Steel, Large Rolled Bar.	Hard Siemens Steel, Large Rolled Bar.
0	0·011	0·018	0·020	0·018	..	0·007	0·010
Seconds 30	0·014	0·015	0·018	0·018	0·000	0·009	0·010
Minute 1	0·018	0·014	0·014	0·023	0·002	0·007	0·011
Hours 1	0·013	0·014	0·013	0·032	0·003	..	0·009
„ 6	0·011	0·011	0·012	0·015	0·007	0·003	0·016
„ 18	0·009	0·007	0·007	0·008	0·003	0·003	0·006
Days 1	0·007	0·006	0·004	0·006	0·002	0·002	0·005
„ 2	0·004	0·005	0·003	0·003	0·002	0·002	0·004
AVERAGE	0·013	0·018	0·023	0·031	0·007	0·004	0·015

Time from Commencement of Experiment.	Electro-chemical position of the unstrained metal, Positive, except where otherwise specified. Electromotive Force in Volt.							
	Description of Metals.							
	Soft Bessemer Steel.	Hard Bessemer Steel.	Soft Cast-Steel.	Hard Cast-Steel.[3]	Silicon Steel.	Aluminium Steel.	Nickel Steel.	Copper Steel.
0	0·010	..	..	0·013	0·009	..	0·009	0·030
Seconds 30	0·009	..	..	0·011	0·010	..	0·006	0·038
Minute 1	0·006	..	..	0·012	0·011	..	0·005	0·044
Hours 1	0·031	0·004	0·004	0·059	0·004	0·005	0·028	0·012
„ 6	0·024	0·007	0·006	0·058	0·001	0·002	0·014	0·009
„ 18	0·011	0·004	0·003	0·014	0·003	0·002	0·009	0·002
Days 1	0·010	0·004	0·004	0·011	0·003	0·002	0·007	0·003
„ 2	0·009	0·006	0·003	0·003	0·003	0·002	0·004	0·004
AVERAGE	0·019	0·006	0·005	0·035	0·005	0·003	0·002	0·017

FIG. 46. EFFECT OF TORSION STRESS ON THE CORROSION OF METALS IN SEA WATER (172

Index Number.	Description of Metals.	Normal Tensile Strength of Unstrained Metal.				Physical Properties of Strained Metal after Torsional Stress.				Increased Rigidity Per cent. due to Torsional Stress.
		Original Diameter of Test Piece in Inches.	Breaking Stress Tons per Square Inch.	Elongation per cent.	Reduction of Area per cent.	Stress imposed on the Metal represented by Angle of Torsion in Degrees.	Breaking Stress Tons per Square Inch.	Elongation per cent.	Reduction of Area per cent.	
B. W. C.	Wrought-iron (rolled) . . .	0·750	22·83	30·3	42·3	180	30·02	5·0	21·4	31·49
	" " (hammered shaft) .	0·793	22·00	25·3	27·4	180	27·52	2·0	1·6	25·09
	Siemens steel " " .	0·798	43·70	20·0	31·6	180	46·08	15·0	37·6	5·44
	" " " " .	0·798	24·60	27·0	33·6	180	30·00	21·3	55·8	21·95
	Bessemer steel " " .	0·798	57·86	26·7	47·2	180	42·18	13·3	23·0	11·41
	Soft Siemens steel . . .	0·559	23·90	28·0	35·1	180	32·93	16·0	24·4	14·05
	Hard " " . .	0·875	50·07	14·0	43·4	180	54·36	14·0	21·6	8·57
	Soft Bessemer steel . .	0·559	26·29	40·0	53·9	180	31·16	30·0	56·8	18·52
	Hard " " . .	0·875	45·54	20·0	32·8	180	53·72	14·0	21·6	17·96
	Soft cast-steel	0·559	31·96	17·0	29·4	180	37·40	14·0	18·4	17·02
	Hard " "	0·872	43·75	2·7	3·2	45	49·74	2·0	3·1	13·69
	Silicon steel	0·559	31·12	37·0	48·6	180	41·40	24·0	44·4	21·34
	Aluminium steel . . .	0·559	33·39	32·0	40·8	180	38·68	20·0	30·8	15·84
	Nickel " . . .	0·559	37·59	38·0	53·8	180	44·83	18·0	33·2	19·26
	Copper " . . .	0·875	35·72	20·0	26·5	180	41·48	24·0	44·4	16·13
	Chromium " . . .	0·875	45·69	none	none					

Large bars.

FIG. 47. EFFECT OF TORSION STRESS ON THE PHYSICAL PROPERTIES OF METALS IN FIG. 46. (172)

A third and final set of experiments was carried out by Andrews on the influence of flexional stress on corrosion using plates illustrated in Fig. 40. The conclusion to which was that the forging which had been subjected to flexion stress was less 'corrosible' than the 'unstrained' metal in its normal condition. Under conditions when iron or steel is exposed to the influence of hydrogen evolution, Ledebur found that the flexional stress was reduced.(173)

Analysing Figs. 44, 46, 47, shows than an average e.m.f. of 0.016 volts was obtained between the 'strained' and 'unstrained' portions of wrought iron forged shafts under the conditions recorded. In the observations on all these metals, the 'unstrained' metal was found to be in the electro-positive position corresponding to the zinc element in a galvanic couple. This factor indicated that the 'unstrained' plates were being more acted upon by the electrolyte than the plates strained by flexion. Andrews illustrated quite convincingly in this work that not only is the corrosion of metals effected by stress, but it also varies according to the nature and extent of the strain applied. It might have been considered that metals under stress would be more liable to increased corrosion than when in their normal state. This is when 'strained' is considered separately from 'unstrained' metal. However, when the strained metal is in galvanic contact with the unstrained metal in any solution, an increased total corrosion occurs from the galvanic action which arises, and which Andrews showed was consequent on the difference of potential between the two.

5.5. ACID INFLUENCES

The resistance offered by different varieties of iron and steel to the corroding effect of diluted acids depends greatly upon the nature and quantity of the elements associated with iron.

Some experiments conducted by Ledebur(174) with various kinds of iron showed that the resistance to the action of dilute sulphuric acid increased with the proportion of carbon. The acid had a density of 1.05, the

metal being employed in the form of cubes, and was allowed to remain at rest for sixty-five days.

Andrews also showed that iron containing a considerable amount of carbon was less readily attacked by nitric acid than pure iron.

There have been a number of contradictory statements regarding the influence of different proportions of carbon, and carbon in different states of combination, on the corrosion of iron and steel in air and water, but on this subject not a great deal was published at all.

Percy stated[175] that hardened steel is much less readily acted upon by acids than the same steel when softened, and quoted an experiment by Daniell in support of his view.

Steel when magnetised, Andrews found to be more readily corroded by acids, than when unmagnetised. His experiments showed that magnetism diminished the passivity of steel in nitric acid.

The fact that iron in any form, whether wrought or cast, and also steel, is readily dissolved by a variety of acids was recognised by Percy in 1861.[176]

Mallet observed that cast iron rich in silicon was not attacked by hydrochloric acid and this observation was confirmed later by Tilden.[178] Iron containing upwards of 10 per cent silicon was found to resist acid attack exceptionally well and he proposed to employ this metal for the production of pipes, taps and other articles in chemical works. He observed that when cast iron containing considerable phosphorus was dissolved in acids, the residue contained phosphorus in combination with iron, in some form which he did not state, which was not attacked by ordinary solvents.

Though the usual forms of iron and steel are attacked by dilute acids, and by strong hydrochloric acid, they were observed to be not dissolved by either strong sulphuric acid or by strong nitric acid.[179] Andrews showed that[180, 181, 182] when strong nitric acid acts on iron, the metal assumes a passive state. He found that the passivity in nitric acid of 1.42 density is regulary diminished as the temperature rises, until at about 90°C, the

point of transition from the passive to the active state is reached.

Akermann observed[183] that where rusting had already begun, the change from the first formed ferrous compound to "ferric hydrate", was attended by the release of an active acid, which was in a condition to act in the formation of fresh rust.

CHAPTER 6

GLOBAL DEVELOPMENTS

On the Continent, similar investigations[184] on the relative oxidability of cast iron, steel and wrought iron were also taking place.

Grüner[184] regarded the assumption that the relative oxidability by the examination of acidulated water was unwarrantable. He considered that there was no reason why this should be equivalent to the action of moist air or of salt water.

To show this, he took twenty-eight polished plates of steel and iron, of different degrees of purity, and hardness. They were fixed by their four corners into a wooden frame, so that they could be easily manipulated. Each plate was carefully weighed, both before and after the experiments. In eight days, the steel plates had lost from three to four grains per plate, and very surprisingly, he found that those containing chromium were attacked the most, and those containing tungsten more than those made of ordinary steel.

Those of cast iron, corroded less than the steel and wrought iron, and amongst them those containing 20 per cent of manganese less than grey iron. He found that sea water attacked iron, dissolving it, like acidulated water and that it attacked cast iron more strongly than steel. Unlike moist air, it attacked cast iron more strongly than steel. Perhaps the most unusual feature to come from this work was that chromium was found to be detremental to the corrosion resisting properties. He does not however, give any details regarding the percentage present. It may well be that the quantities involved were particularly insignificant.

Experiments on similar lines, were carried out later in America.[185,186] Although these experiments, carried out by Howe were not published in detail they do confirm many of the findings found by British scientists. He found that soft steel corroded more than wrought iron in sea water in all cases, but not in other media. The inference that can be drawn from this work is

that the difference in the rate of corrosion between wrought iron and soft steel is rarely great except in marine boilers. Also that the ratio of corrosion of given soft steel to that of wrought iron may vary greatly with the conditions of exposure.

In Germany, during the late nineteenth century, probably the major publication was on the relative corrosion of wrought iron and steel was by Otto and published in Stahl und Eisen.(187)

The major work on this subject had been carried out in England and Otto in his publication stated that this work had been brought about after reading the paper by Parker,(153) given before the Iron and Steel Institute in May 1881. He mentioned that considerable discussion took place about the results of the investigation between himself and Krupp, who asked him to carry out his own investigations.

In the experiments, metals of different percentages of manganese and carbon, were chosen and only open-hearth steel and 'weld iron' were chosen. The work was comprehensive, the important conclusions being that under boiler conditions, where the action was least, the relative degree of rusting varied little being nil for unannealed spring steel, and 0.50 per cent in annealed soft steel. The greatest differences he found, were under warm moist air conditions. This was a set of conditions that none of the other experimenters had investigated. Spring steel was observed to rust most, and the loss in weight was about 8 per cent. The length of time for this test was not stated. Otto, in concluding, draws attention to the changes in composition of steels which had taken place since the time of the actual tests, and this may well have been the reason that none of the British scientist followed this up, thinking the comments and results outdated. Yet it is surprising that Andrews, and the other workers who undertook investigation in the last decade of the nineteenth century did not consider the effect of warm moist air in their comprehensive studies. Andrews was basically a 'practical' man and it may well have been that the results given in Stahl und Eisen did not come to his attention.

Another paper of significance, which appeared in Stahl und Eisen, was given by Thörner.[188] He analysed a large number of samples of rust taken from the surfaces of rails laid in tunnels. He found that sulphuric acid was always present in considerable quantities and that the gas es escaping from locomotives, besides containing "sulphurous anhydride," contained large quantities of sulphuric acid, and that it was to this cause, that the undue rate of oxidation of ironwork in railway tunnels was due. He found that those parts of the iron work which were wet by dropping water, were less oxidised than other parts. The presence of sulphuric acid had been detected by other workers, but Thörner was the first to comment on the relative oxidation of ironwork in this manner.

Observations of a number of American scientists, and engineers on the corrosion of buildings and bridges have already been stated.

CHAPTER 7

CORROSION OF NON FERROUS METALS

7.1. COPPER

Copper was one of the more important non-ferrous metals in the nineteenth century, primarily because of its application as a ship sheathing material. Scientific attention became focussed upon it during this period because of the corrosion and pitting it endured in sea water and because of its action when in contact with other metals, particularly iron and zinc.

The British Association Report of 1835 [189] contains a reference from Edmund Davy about the condition of harbour buoys at Kingstown in Ireland.

Copper had been used as a sheathing material, and the whole surface of each buoy was sheathed with copper, except the bottom and about three inches of the smaller end. This was covered with lead, fastened to the copper by nails. A bolt passed through the whole length of the buoy, and was terminated at each end by a shackle.

All the ironwork at, and near the base of the buoys, was very corroded, but Davy was able to appreciate that the corrosion of the iron work was due to an electrical action produced in sea water by the contact of the iron with the copper.

At this time, 1835, the durability of copper for bolts and ship-sheathing, was an object of considerable national importance and investigations that had taken place at earlier dates now took on a new significance.

Mushet [28] described a series of experiments he had performed some thirteen years earlier on the immersion of copper for bolts and ship sheathing in hydrochloric acid, as a test of its durability.

Small quantities, presenting equal surfaces of pure copper and unrefined copper, were separately immersed in equal weights of hydrochloric acid for forty-eight hours. After this period, the acid was poured off,

and the copper was washed repeatedly and thoroughly dried. The pure copper had lost 5½ grains in 100, but the unrefined copper, on being weighed, appeared to have gained half a grain.

Mushet considered that this gain, could have been caused by a mistake in the weighing or a portion of unexpelled moisture remaining in the porous flakes of the copper.

In further experiments, repeating the same procedure, he obtained a 30 per cent loss for unrefined copper against 46 per cent for pure copper. To clarify the position, he obtained losses of 17 per cent for the unrefined against 45 per cent on a third test. Although the results of these tests give widely differing values, they do give an indication that the unrefined copper had better corrosion resisting properties than pure copper. This could well be due to tin that is normally present in unrefined copper.

At this stage of corrosion testing, it was rare for any experimental data to be given. Mushet gives no indication as to whether the samples in each case came from the same specimen, or whether the samples were cleaned before or after the experiment. An inconsistent experimental technique could well account for the divergent results he obtained. There is some doubt whether Mushet was motivated by Davy's paper of 1824.(76) According to Mushet's statement, one can calculate that these experiments were carried out in 1822, some two years before Davy's publication.

The important practical problem in the mid nineteenth century, was not the influence of hydrochloric acid on copper, but that of sea water.

In 1851, James,(190) decided to investigate the action of sea water on copper containing phosphorus, and found that the phosphorus had a little influence in improving the resisting properties.

Also in that year, Hayes(191) investigated the effect of corrosion on an alloy of copper and silver. He found that the addition of one ten-thousandth part of silver was sufficient to improve the alloy's corrosion resistance.

Many of the experiments carried out during this period were unrelated

and it was only with the publication by Percy in 1861, of his book on Metallurgy, that many of these facts were drawn together and presented in such a way that they were comprehensible to the practicing scientists and engineers.

In this work, he illustrates how the loss per sheet per annum sustained by sheathing varies so considerably when in contact with salt water. This variation being attributed to differences in the quality of the copper and more particularly to the presence of lead, bismuth and antimony. These facts were substansiated one year later by Abel and Field[192] in 1862.

By this time, however, sheathing had become a matter of smaller importance than formerly, because of the increase in the number of iron ships.

In 1866, Calvert and Johnson[193] published experimental results on the action of acids on copper and brass. They found that an alloy of about equal weights of copper and zinc, immersed in strong hydrochloric acid at common temperatures releases in a few days, nearly the whole of the zinc, leaving the copper behind in a spongy state. Pickering[194] much later, in 1878, carried out similar experiments. In both of these cases, the experiments were carried out using cubes of cast metals. Further experiments were carried out along similar lines by Tilden[195] in 1886, but in using 1 mm. sheet material instead of cube, he stumbled across a fact of considerable significance, that of stress-corrosion. He did not appreciate this in his paper:-

"I found that sheet brasses of various composition resist the action of strong hydrochloric acid in the cold better than would appear _ _ _ .

"But a very curious fact presented itself, I found that if the sheet was bent, a very rapid action set in at the bend, resulting in the disintegration of the metal at that part."

The action of weak hydrochloric acid and of solutions of chloride, was observed by Calvert and Johnson to be different from that of strong hydrochloric acid.

The experiments recorded in their paper relate to the action of sulphuric, nitric and hydrochloric acids of various strengths on copper, zinc and tin, and in several brasses and bronzes. Unfortunately, this material, as used in industrial applications was rolled as distinct to their cast specimens and consequently the results they obtained did not have the same useful significance they could have had.

However, later work by Tilden[195] in 1886 using rolled specimens, in general confirmed the results of the experiments by Calvert and Johnson and also much earlier work by Mushet[28] in 1822.

In this work, Tilden found that in three brasses tested, the constituent metals were dissolved away in proportions which are practically the same as those in which they occur in the alloy.

When the total amount of attack is considered, the alloy with least copper was better adapted to withstand the action of weak hydrochloric acid than any of the three which contained more copper.

7.2. ALUMINIUM

Aluminium and its alloys which today play such a prominent part in industrial life, where during the nineteenth century, suspect materials.

Winkler in 1877, stated in Dingl J.[196]

"Hitherto, aluminium has been considered to be a metal easily attacked by the atmosphere, and by weak alkalis and acids. This idea has prevented its employment to any great extent, and yet zinc, which is quite as easily attacked, is one of the most useful metals in the arts."

The author states that he instituted experiments on objects in aluminium exposed to atmospheric action, but a storm destroyed the equipment.

By 1890, aluminium was begining to be recommended for[31] certain architectural work on account of its lightness and its assumed permanent lustre. It was considered to be unaltered by exposure to the air, to the action of water, hydrogen sulphide and only slightly by dilute acids.

H. C. Russell, who was a Government Astronomer, decided to try aluminium cups for a rain gauge, but found that they were so quickly corroded that he had to 'relinquish the metal'. (SEE REF 197).

When Liversidge[197] heard of this, he decided to investigate the material and to try and determine for himself, which of these diverse reports regarding the metal was true.

He made two shallow dishes of 1/25 inch gauge metal, of the best commercial quality, and exposed them on the roof of his laboratory for 54 weeks.

The metal was then made into basins to catch the rain water and to add salts. The metal very soon lost its brilliancy, and became somewhat rough and speckled with grey spots mixed with larger light patches. He states:-

"Contrary to my expectations, the cups had not lost weight, but had even increased. One, weighing 13.91 grains, had increased by 0.104 grains and the other weighing 13.865 grains, increased by 0.080 grains. After boiling in water for some hours, and rubbing, the first still showed an increase of 0.077 grains, and the second 0.055 grains."

One important factor that Liversidge did not investigate, was the relative types of corrosion between a shielded and unshielded aluminium surface when exposed to atmospheric conditions. Both the form of the corrosive product and the weight loss would have been seen to be distinct.

Other atmospheric tests were carried out by Wilson.[198] He endeavoured to determine the effect of atmospheric exposure on the electrical conductivity of a range of aluminuim alloys.

The specimens he used were in the form of wire, supported on a wooden frame for a period of 13 months exposure in London.

He appreciated fully, how the relative position of metals in the electrochemical series influenced corrosion rates. He stated:-

"The position of aluminium in the electrochemical series with respect to the other substances in the analysis is as follows:- Al, Mn, Zn, Fe, Ni, Cu, Si.

We should expect to find that copper, widely separated as it is, would be effective in the production of corrosion. This is found to be the case, the effect increasing with the percentage of copper. Nickel is well separated from aluminium in the series, and alone, has considerable effect, but if alloyed with copper, the conductivity has slightly increased during exposure."

Apart from the influence of the atmosphere on the corrosion of aluminium, experiments were carried out to investigate the action of distilled, filtered river water and of spring water upon carefully cleaned strips of aluminium sheet.

Donath[199] boiled strips from the sheet for 48 hours in beakers in contact with the water under test. In the case of distilled water, the surface of the metal remained bright except where it had been more or less exposed to the air, and here it was covered with a faint veil of white deposit. The strip lost only 6 m.g. on 8.3832 g.

Comparing these results with those of Liversidge for atmospheric corrosion, in this case the Al_2O_3 formed in quantity during atmospheric corrosion would not be present and would consequently result in a weight loss.

The filtered river water, and less marked, the spring water, soon caused visible corrosion and he reported that rough dark grey, black or brown patches with a deposit were formed.

Experiments also took place on the behaviour of aluminium towards a number of liquids with which it might come into contact when made into canteens, cooking vessels and surgical instruments.

Lubbert and Roscher (SEE REF 200) considered that the use of aluminium would be detrimental "to liquids intended to pass into the human body."

However, they did not appear to have made any quantitative estimations but confined themselves to qualitative observations. Also they appear to have worked exclusively with aluminium foil and not with commerical material.

Lunge[200] using commercial material, did carry out quantitative tests

and observed that the action of coffee, tea and beer, is zero, or practically so, that of brandy is extremely slight and the worse case, acetic acid, was less than 5 mg. per 100 sq.cms. in six days.

He concluded that there was not the slightest danger of any injurious action upon the human body by traces of aluminium compounds.

The action of beer on aluminium was also investigated by Kobert.(201)

He found beer stored in aluminium vessels takes up 8 mg. of the metal per litre.

However, as distinct from zinc, minute quantities of aluminium by-products even if they are present, do not cause poisoning and so consequently no further investigation on the action of beer appears to have taken place.

An interesting example(202) of galvanic action between steel rivets and the aluminium hull of a yacht is illustrated in fig. 48. The yacht had been in service for about 4 years when the photograph was taken.

7.3. ZINC

In 1830, A. de la Rive(203) showed that distilled zinc dissolves very much more slowly in dilute sulphuric acid than the commercial substance. He showed this to be due to the removal of other metals by distillation. The dissolution of commercial zinc was ascribed to the formation of voltaic couples of zinc with the various impurities, and the strength of acid which acts most readily upon the metal was shown to be that which has the greatest electrical conductivity.

It thus seemed natural to suppose that pure zinc would not be acted upon by pure sulphuric acid, but that if a third substance were present whether in the metal or in the acid, dissolution would be effected owing to the formulation of an 'electric circuit'.

Reynolds and Ramsay(204) in 1887 found that after preparing highly purified zinc:-

"the sublimed metal _ _ _ was nearly unacted upon by sulphuric or hydrochloric acid."

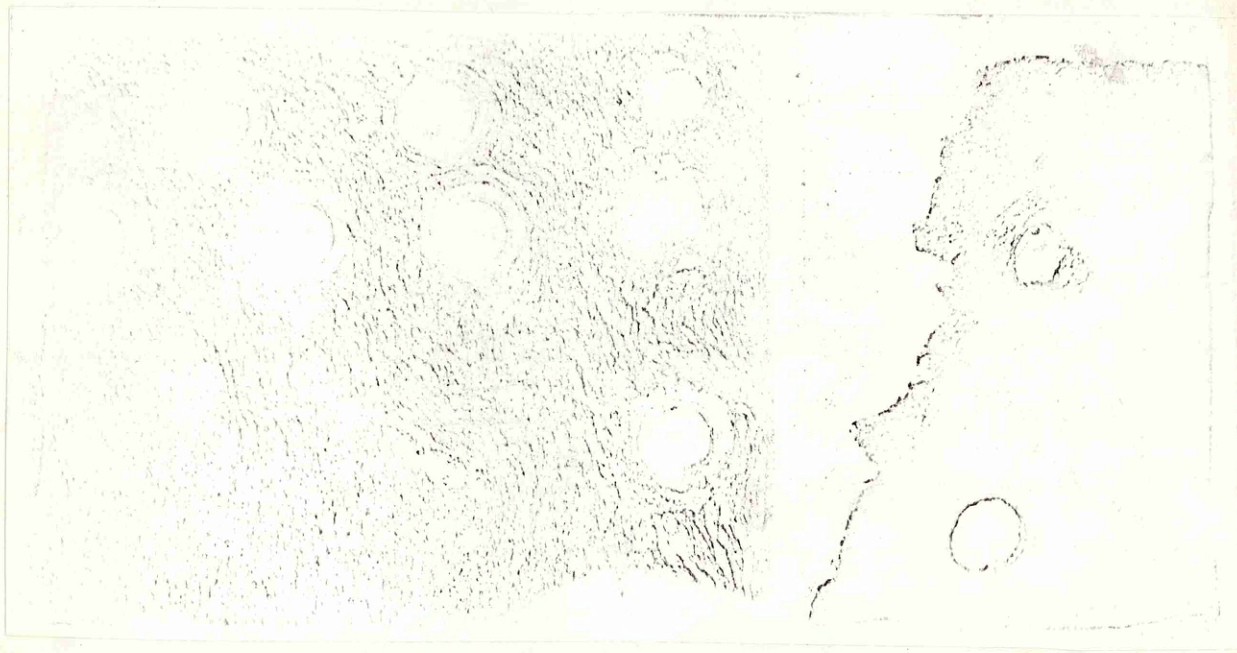


FIG. 48. GALVANIC ACTION BETWEEN STEEL RIVETS AND A YACHT'S ALUMINIUM HULL (202)

Observations on the nature of the metallic surface were made in 1866, by Calvert and Johnson. They noticed:-[193]

"the irregularity of the action of sulphuric acid on zinc, depending _ _ _ upon the peculiar state of its surface.

"Thus we have found," they say, "that cubes, which had been made of the same zinc, but at different times, were acted upon more or less by the same acid when placed under the same circumstances; and these observations, gradually led us to the discovery of a very curious fact, that a perfectly clean surface of zinc will become after a few days, sufficiently oxidised by contact with air to modify, in a very marked degree, the action of sulphuric acid upon it. Thus, if a cube of zinc recently filed is placed in sulphuric acid diluted with nine equivalents of water, the action may be considered as null; whilst if the same cube be gently heated in contact with air and allowed to cool, and be then placed in the same strength of acid, the attack is ten times greater."

From this paragraph, it would appear that roughness, not oxidation of the metallic surface, is the cause of the increase in dissolution rate. Superficial oxidation probably caused only a momentary influence, since the oxide would be instantly dissolved by contact with the acid, whereas increased roughness produced by the formation and subsequent dissolution of the oxide, would increase the rate of dissolution of the metal quite considerably.

Pullinger, later in 1890[205], found that dilute sulphuric acid had very little action on zinc, provided that the acid was boiled for several hours and the metal was made perfectly smooth.

Observations on the behaviour of strong sulphuric acid on zinc were made by Muir[206] in 1880. He found that when zinc was boiled with strong sulphuric acid, a point was reached at which the evolution of gas was observed 'to slacken' as sulphur began to separate.

Müller,[207] writing in Zeit f. angew Chem, in 1888, reports about the 'remarkable' corrosion of zinc pipes. These pipes carried the rain water off the Royal Castle that was at Brunswick. The pipes which drained the copper covered dome, were the only ones to corrode rapidly. Müller, fully appreciated the significance of this, and correctly attributed it to galvanic action.

7.4. LEAD

Lead piping has been used for a considerable time as a means of conveying drinking water to customers. An anonymous author[208] mentions as an example of the long periods of useful service which lead is capable of giving, that some pieces of cast piping in the Latin Department of Columbia University bear the names of the Roman Emperor Vespasian (A.D.69-79) and the maker.

With many supplies the quantity of the water is not appreciably affected as a result of its contact with the metal.. There are instances, however,[30] in which the composition of the water is such that it attacks the piping and becomes contaminated with lead. In a number of these cases[30] the quantity of lead taken up by the water has been sufficient to give rise to lead poisoning among consumers.

Early in the study of the action of natural waters upon lead[29] the character of the water as indicated by hardness or softness, was considered to be important. Various workers have sought to assess the importance of possible factors by the addition of distilled water to the substances considered effective in checking the action.

About 1850, Penny, who took a considerable part in an investigation of the Loch Katrine supply to Glasgow, wrote:[30]

"It is not a little curious to observe how suddenly the views of chemists have oscillated and changed. At one time, it was maintained that spring waters were most powerful in corroding lead. Guyton-Morveau, Christison, and others on the contrary inferred that the corrosive power

of a water was in direct proportion to its purity and that certain saline ingredients in spring water were a means of preventing its action on lead."

The contradictory opinions are centred around generally held, but opposing views that at one time, soluble sulphates and phosphates were regarded as the most powerful protective agents and the nitrates and chlorides the most active saline promoters. At another, waters which are alkaline and those which contain a notable quantity of organic matter or of carbonic acid gas are considered to be the most energetic in their corrosive powers.

Nichols,[209] in a long essay expresses the opinion that any attempt to fix a limit to the amount of saline substances or of any particular substances which must be present in order that there should be no action on lead, must be fruitless.

It appears reasonably certain that much of the contradiction regarding the effects of various constituents arose in two ways.

Distilled water is not a simple substance unless great care is taken to render it so. Two batches of water distilled from the same source may differ considerably, whilst satisfactory comparison of results obtained after additions of salts, made by two independent authors to distilled water prepared under different conditions may not be possible. The importance of this point is brought out by Müller,[210] who made a comparison of three fractions of the distillate of water which originally contained 0.00015 per cent ammonia. He recognised the importance of the fact that the boiling of water followed by rapid cooling does not render the liquid free from oxygen, nitrogen or carbon dioxide. Most of the ammonia and carbon dioxide passed over in the first fraction, much less appeared in the second and less still in the third. The first fraction kept for 24 hours in a closed filled flask, gave scarcely any action on a strip of lead placed in it. The action of the second and third fractions was quite distinct, the strips being visibly attacked in 24 hours. He stated:

"The attack was, however, not so strong in the time as it would have been had a carefully prepared distilled water been used."

The distillation of a spring water similarly gave three fractions, but in this case, the first and third did not attack lead so markedly as the second.

Von Stalmann[211] in 1866, distilled water from Oker (Brunswick) and found differences in the behaviour towards lead in three successive fractions. The first fraction, containing most of the ammonia, appeared most active whilst the second and third were almost completely indifferent. Von Stalmann considered that when a critical amount (0.0001 to 0.00015 per cent) of ammonia was exceeded, the attack was retarded.

Houston[212] draws attention to the same effect observed in distilling a hard limestone water. The first fraction was distinctly acid, containing free ammonia and had practically no corrosive power on lead, but dissolved lead to a marked extent. The third was practically neutral and had generally no solvent power, but corroded the metal quite vigorously. The second fraction, occupied an intermediate position as regards composition and properties.

Garrett[213] however, emphasizes that in distilled water there appears to be no connection between alkalinity, acidity or neutrality of a distilled water and its action on lead. He found that some distilled waters act vigorously on lead. Those which have an alkaline reaction are more active but alkalinity in itself is not an indication of inactivity.

In making additions to the samples of distilled water to judge the protective or active effect exerted, sufficient care has in general to be taken to ensure that other conditions remain the same.

Ruzicka[214] in wishing to demonstrate that carbon dioxide does not cause an increased attack, filled three cylinders with distilled water. Into the first no carbon dioxide was admitted, but the lead test piece was inserted and the full cylinder stoppered. Through the second a current of the gas was passed for five minutes and the third was treated with the gas

for 24 hours. A marked reduction of attack was reported as a result of the passage of the gas. At least one explanation seems to be that the available oxygen in the three cases was not the same. In the twentieth century, Zink[215] also made a series of similar experiments in which additional carbon dioxide was passed into distilled water. Like Ruziska,[214] he found a considerable reduction in the quantity of lead passing into solution, but realised that the oxygen content had probably been altered by the passage of the carbon dioxide.

It has been generally accepted[29] that air or oxygen is necessary to allow cold distilled water to act appreciably upon lead. Yorke[29] in 1834, agreed with Guyton-Morveau[216] that water deprived of, and kept from contact with air, is unable to act upon lead. The latter worker remarked that distilled water acts on lead without the assistance of agitation even in glass vessels in which the possibility of galvanic action is excluded. Admission of air to previously de-aerated water enables the action to recommence. The nature of the product clearly shows oxidation to have taken place without decomposition of the water and Guyton-Morveau considered that a hydrate is formed. This point appears to have been so generally accepted that de Saussure[216a] in 1836, considered the possibility of using the reaction as a basis for an eudiometric method of determining oxygen by shaking the gas with water in the presence of lead. Since then, it has been shown that the presence of oxygen is essential to the action.[216, 217]

Traube[218] showed that lead is not attacked by air dissolved in absolute alcohol. When water is added to the alcohol, the attack begins and increases with further additions up to 50 per cent, when the action is nearly as rapid as with pure water. According to Traube[218] the action of water in the presence of air is dependent on the formation of hydrogen peroxide and cannot be satisfactorily explained by assuming that nascent hydrogen is produced and subsequently oxidised by dissolved oxygen.

Garrett[219] considered that the purity of the metal has little effect on its behaviour towards water. He conducted experiments using strips of lead bent to form half loops, each loop being completed by adding a similar piece of a second metal. These hoops were immersed in (A) distilled water for 12 hours, (B) distilled water faintly acidic with acetic acid, for 3 hours. (C) 0.5 per cent acetic acid for 12 hours, and (D) a peaty water from Dartmoor for 12 hours. The figures in fig. 49 are comparitive only, that for lead being taken as 100.

Lindsay[220] considers that, in practice, contact with iron pipes, solder, etc., is an important factor in assisting the attack on lead by water. In his paper he quotes an opinion that galvanic action is a most powerful agent in promoting the corrosive action of certain waters upon lead.

Various workers[221, 222] considered that the presence of foreign metals in lead would be possible sources of galvanic action which might in certain circumtances, give rise to an accelerated attack of the metal.

Brown[221] expressed the opinion that tinned pipes and pipes made from re-melted lead, are more dangerous in use than those made from virgin lead.

Carles[222] made some experiments with lead containing additions of 1 - 10 per cent tin, 0.1 - 0.5 per cent fine silver, and 0.1 - 0.5 per cent of a mixture, of copper and silver and concluded that in general, the purer the metal the less the attack which it suffered. In an analysis of these various conclusions, the influence of earlier work by Davy,[76,77] on galvanic action and impurities in copper can be seen. The question that appears to have been prominent in many minds, was 'do the laws that govern the galvanic action and influence of impurities in copper apply similarly to lead.'

Muir,[223] compared the action of water upon three samples of lead:- (a) a very pure lead containing only traces of manganese, iron and zinc.

	A	B	C	D
LEAD + SILVER	120	133	-	300
LEAD + COPPER	108	150	-	150
LEAD + IRON	100	7	-	-
LEAD + ALUMINIUM	16	0	7	-
LEAD + TIN	14	0	7	70
LEAD + ZINC	6	5	-	70

FIG. 49 COMPARATIVE CORROSION IN DIFFERENT SOLUTIONS. CORROSION OF LEAD TAKEN AS 100 (227)

(b) a commercial sample which contained small amounts of antimony and tin very little iron and traces of aluminium, but no copper, manganese or bismuth; (c) a sample having generally the characteristics of (b) except that it contained copper.

Striking differences in behaviour were found. Using water and different dilute saline solutions, less lead was dissolved in almost every instance from sample (b) than from sample (a) while sample (c), the composition of which was almost identical with that of (b) gave the greatest amounts of dissolved lead. Furthermore, mechanical treatment alters the behaviour of the lead towards saline solutions to a remarkable degree. Rolling together several sheets of the pure foil (a) into one compact sheet materially decreased the solubility in a nitrate solution; with sample (b) similar treatment increased the solubility in ammonium nitrate solution by about 18 times, whilst hammering several sheets together had the opposite effect.

The influence of material strength on corrosion was very rarely considered and this appears to be the first instance that it was considered in relation to lead.

Outbreaks of plumbism due to water supply, appear in general to have taken place in towns or districts using comparatively soft water. Numbers of examples are cited in the literature,[30] however, which show that softness alone, is not a definite criterion of the ability of a natural water to attack lead.

Crook, Odling and Tidy[30] investigated the water supply in a number of towns using soft water. They found that the power of a soft water to act continuously on lead services is not related to the power to act on clean new lead.

The analysis quoted by White[224] for the Sheffield high and low supplies also illustrates the same fact. The high level supply had caused the trouble, whereas the low level was satisfactory. The former was acidic

in reaction and the acidity was intensified on concentration by evaporation.

Between the period 1875, and 1877, Muir published a series of papers on the solvent action of various saline solutions upon lead.

In these papers, he determined the circumstances conditioning the solvent action of the saline solutions he had experimented with.[225,226,227]

In the first paper[225] he examined the nature and the quantity of the salts in solution with a view to ascertaining their effect on lead. Pieces of clean bright lead were suspended in these various solutions for different lengths of time, and the amount of lead which was dissolved was estimated at different intervals. From the results he obtained, he concluded that nitrates, if present alone even in small quantities, cause water to exert a very marked solvent action upon lead. The presence of other salts - sulphates, carbonates and chlorides-greatly decreased this solvent action. The amount of lead dissolved increases only slightly after the lapse of twenty-four hours in the presence of these salts.

In his second paper[226] he repeated these experiments endeavouring to determine the quantitive values involved.

In his results he had considerable discrepancies and from this, concluded that the action of dilute saline solution upon lead was materialy altered by what appeared to him to be slight alterations in the conditions of the action.

From the results (fig. 50) it can be seen that in certain cases, the amount of lead dissolved does increase most noticably as the surface exposed is increased, but in other cases, it diminishes.

In the case of distilled water, whether the surface of lead exposed measured 25 or 50 sq.cm. when the action was allowed to proceed for 42 hours, the amount of lead dissolved, was the same. When the action had proceeded for 340 hours, the conclusions to be drawn are found to be considerably effected by the nature of the vessel employed. (see fig 51)

A.—Experiments carried out in corked Flasks nearly filled with liquid, 500cbc. in each.

Nature of Solution.	Grams per Litre.	Surface of Lead exposed in sq.cm.	Total Lead in Milligrams in Solution in the Liquid after								
			42 hours	68 hours	70 hours	138 hours	140 hours	168 hours	336 hours	340 hours	505 hours
Distilled Water	....	25	0·7	..	..	..	..	..	..	1·2	1·5
" "	....	50	0·7	..	..	..	..	..	..	0·9	1·0
" "	....	60	..	0·5	0·5	0·8	0·8	..	..	..	..
" "	....	120	..	0·2	0·2	0·4	0·4	..	..	..	..
Potassium Nitrate	0·132	60	..	0·5	0·5	0·7	..	..	..	..	..
" "	"	120	..	0·2	..	0·4	..	..	..	..	..
" "	"	240	..	..	0·1	..	..	..	..	..	..
" "	0·232	60	..	..	0·7	..	..	..	..	..	..
" "	0·20	25	0·7	..	..	..	..	..	..	1·2	1·6
" "	"	50	1·0	..	..	..	..	..	..	1·2	1·5
Ammonium Nitrate....	0·20	25	0·9	..	..	..	..	..	..	1·8	1·8
" "	"	50	1·4	..	..	..	..	..	..	1·5	1·5
Calcium Chloride.....	0·132	60	..	0·4	0·4	0·7	..	..	..	..	..
" "	"	120	..	0·2	0·2	0·4	..	..	..	..	..
" "	"	240	..	0·15	..	..	..	..	..	..	..
" "	0·20	25	..	..	..	..	..	1·3	1·8	..	3·0
" "	"	50	..	..	..	..	..	2·0	2·5	..	2·5
" "	0·232	60	..	..	0·7	..	..	..	..	..	..
Potassium Carbonate..	0·20	25	..	..	..	..	..	traces	0·3	..	0·3
" " ..	"	50	..	..	..	..	..	"	0·3	..	0·3
Ammonium Sulphate..	0·20	25	..	..	..	..	..	0·5	0·7	..	0·7
" " ..	"	50	..	..	..	..	..	0·7	0·7	..	0·7

B.—Experiments carried out in Beakers half filled with liquid (500cbc.) and covered with unsized paper: diameter of mouth of beaker=11·5cm.

Distilled Water	....	25	0·4	..	..	..	..	..	..	0·5	0·8
" "	....	50	0·4	..	..	..	..	..	..	1·2	1·8
" "	....	120	..	1·0	1·0	1·2	1·2	..	..	..	..
" "	....	240	..	1·2	1·2	..	..	..	..	..	..
Potassium Nitrate	0·132	120	..	1·0	1·0	1·2	..	..	..	..	..
" "	"	240	..	1·2	1·2	..	..	..	..	..	..
" "	0·20	25	0·4	..	..	..	..	..	..	0·4	0·5
" "	"	50	0·6	..	..	..	..	..	..	2·2	2·5
" "	0·232	120	..	..	1·2	..	..	..	..	..	..
Ammonium Nitrate....	0·20	25	0·4	..	..	..	..	..	..	2·0	4·0
" "	"	50	0·8	..	..	..	..	..	..	3·5	4·0
Calcium Chloride.....	0·132	120	..	1·3	1·3	1·5	..	..	..	..	..
" "	"	240	..	..	1·2	..	..	..	..	..	..
" "	0·20	25	..	..	..	..	..	1·3	1·5	..	2·8
" "	"	50	..	..	..	..	..	2·0	3·0	..	3·5
" "	0·232	120	..	..	1·5	..	..	..	..	..	..
Potassium Carbonate..	0·20	25	..	..	..	..	..	0·2	0·3	..	0·3
" " ..	"	50	..	..	..	..	..	0·2	0·3	..	0·3
Ammonium Sulphate..	0·20	25	..	..	..	..	..	0·7	1·0	..	1·3
" " ..	"	50	..	..	..	..	..	0·7	1·0	..	1·5

C.—Experiments carried out in Basins full of liquid (500cbc.) and covered with unsized paper: diameter of mouth of basin=14·5cm.

Distilled Water	....	25	0·6	..	..	..	..	..	..	2·0	4·2
" "	....	50	0·8	..	..	..	..	..	..	1·5	3·5
" "	....	120	..	..	1·5	..	..	..	..	..	..
Potassium Nitrate	0·132	120	..	..	1·5	..	..	..	..	..	..
" "	0·20	25	0·8	..	1·6	..	..	..	..	2·8	6·0
" "	"	50	1·1	..	..	..	..	..	..	2·8	3·5
Ammonium Nitrate....	0·20	25	1·0	..	..	..	..	..	..	8·0	16·0
" "	"	50	1·3	..	..	..	..	..	..	10·0	16·0
Calcium Chloride.....	0·132	120	..	..	1·8	..	..	..	..	..	..
" "	0·20	25	..	..	..	..	..	2·0	3·0	..	5·5
" "	"	50	..	..	..	..	..	2·5	3·5	..	4·5
Potassium Carbonate..	0·20	25	..	..	..	..	..	0·5	0·7	..	0·7
" " ..	"	50	..	..	..	..	..	0·7	0·9	..	0·9
Ammonium Sulphate..	0·20	25	..	..	..	..	..	2·5	9·0	..	16·0
" " ..	"	50	..	..	..	..	..	2·5	7·5	..	12·0

D.—Experiments carried out in Corked Flasks nearly filled with liquid (500cbc.) through which a stream of air was continually passed.

Nature of Solution.	Grams per Litre.	Surface of Lead exposed in sq.cm.	Total Lead in Milligrams in Solution in the Liquid after								
			42 hours	68 hours	70 hours	138 hours	140 hours	168 hours	336 hours	340 hours	505 hours
Distilled Water	....	25	..	..	..	..	..	..	..	1·5	2·0
Potassium Nitrate	0·132	25	..	..	..	..	..	..	..	1·2	1·5
" "	"	240	..	0·8	..	..	..	..	..	..	..
Calcium Chloride.....	0·20	25	..	..	..	..	..	3·5	3·5	..	3·5
" "	"	50	..	..	..	..	..	0·5	0·5	..	0·5?
Potassium Carbonate..	0·20	25	..	..	..	..	..	0·4	0·6	..	0·6
" " ..	"	50	..	..	..	..	..	0·5	0·5	..	0·5
Ammonium Sulphate..	0·20	25	..	..	..	..	..	1·3	3·0	..	5·0
" " ..	"	50	..	..	..	..	..	0·7	1·3	..	2·5

FIG. 50. ACTION OF VARIOUS SALTS ON LEAD (226)

In closed flasks, the amount of lead dissolved slightly decreased with increase of surface exposed, in beakers it can be seen that there was a very marked increase in lead dissolved with increase of surface exposed, while in basins, there was an increase of surface which was associated with decrease of solvent action. From the experiments carried out in beakers, half filled with liquid and covered with porous paper there appears to be generally an increase of solvent action with increase of exposed surface. From these results it appears to be shown that the solvent action of dilute saline solutions upon lead tends to attain a maximum when large surfaces of liquid are exposed to the surrounding air, and when the volume of liquid is large in proportion to the surface of lead exposed.

In his third paper[227] on this subject he investigated the chemical action which occurs when lead undergoes immersion in liquids containing various salts. He found that the lead in solution was greatest in solutions of calcium chloride.

In the production of sulphuric acid, the large chambers used in this process were constructed of lead, and consequently the action of sulphuric acid upon lead was a factor of considerable importance.

With this object in view a study was undertaken by Calvert and Johnson.[228] They instituted a series of experiments to ascertain the action upon lead of sulphuric acids of various degrees of concentration and purity, in different volumes, at various temperatures, and for various periods of time. They made use of two kinds of commercial lead, choosing as types the two extremes in respect of purity i.e. common sheet lead representing ordinary impure lead and a type known as virgin or Derbyshire pig-lead. They also examined the action of sulphuric acid upon chemically pure lead. In these experiments they found that purer the lead in contact with sulphuric acid, the more it was acted upon.

EXPERIMENTS CARRIED OUT IN :-

A - CORKED FLASKS FILLED WITH LIQUID

B - BEAKERS HALF FILLED AND COVERED WITH UNSIZED PAPER. DIAMETER OF BEAKER MOUTH 11·5 CM.

C - BASINS FULL OF LIQUID AND COVERED WITH UNSIZED PAPER. DIAMETER OF MOUTH OF BASIN 14·5 CM.

D - CORKED FLASKS FILLED WITH LIQUID THROUGH WHICH A STREAM OF AIR WAS CONTINUALLY PASSED.

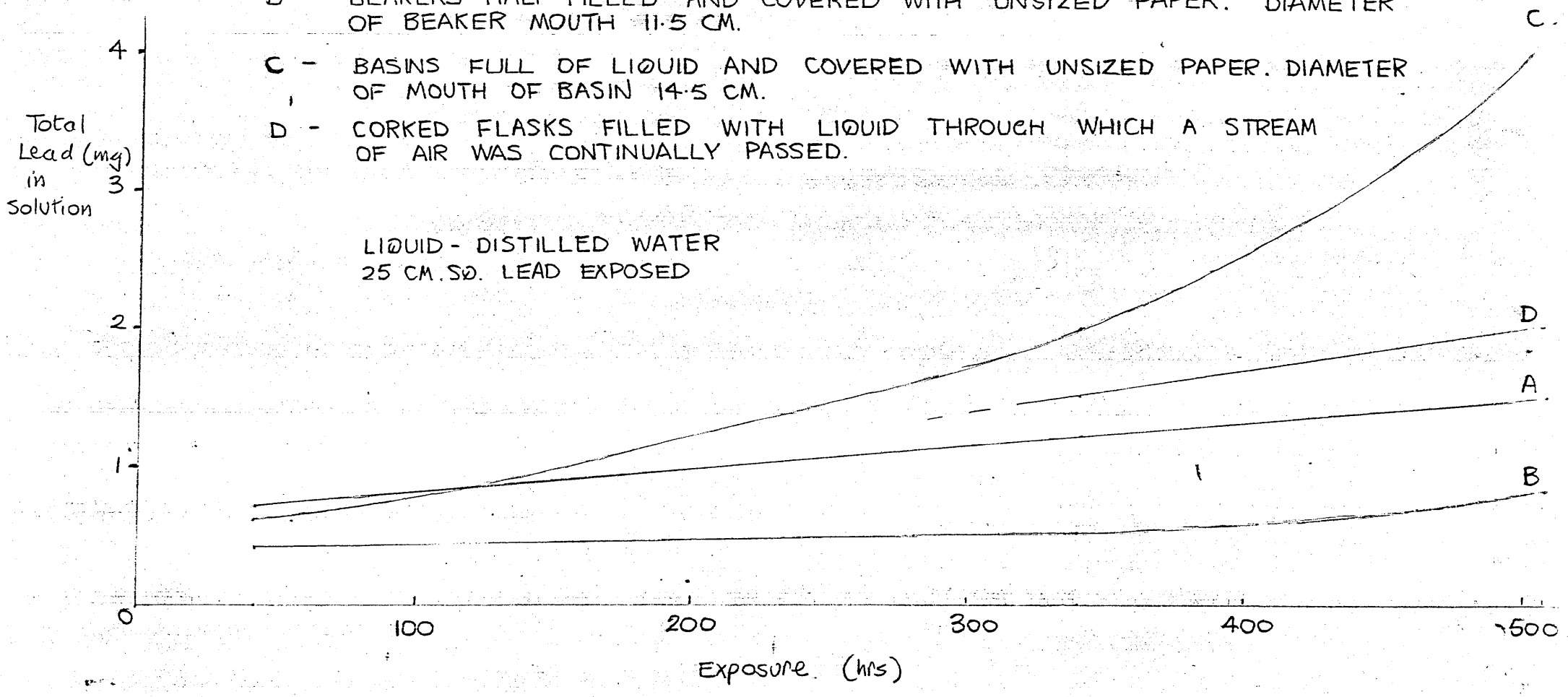


FIG. 51 ANALYSIS OF MUIR'S RESULTS. (226)

They then considered whether the purity of the acid employed had some influence on the results, since they consequently substituted ordinary commercial acid to see if there was a different relative intensity of action. From the results they found that a greater amount of lead was dissolved when it was in contact with the purer acid.

The presence of fluorine compounds in the gases obtained by roasting blendes containing fluorine was also found to be very injurious to the leaden chambers used in sulphuric acid manufacture.(229)

A report in Chem. Ztg.(229) stated that whatever form the fluorine was present in when the gases left the stove, it was in all probability converted to hydrofluoric acid when the hot gases came into contact with the sulphuric acid in the 'Glover Tower.'

Small quantities of hydrofluoric acid were reported to have considerable injurious effects on the lead. No detailed experimental evidence was supplied however.

Apart from the action of acids on lead chambers, investigations were carried out on the action of very low concentration of acids in water when in contact with lead piping.

Carleton-Williams(230) was well aware of the extensive research that had taken place on the action of different qualities of water on lead piping and decided to extend the research a stage further. The experiments were made with the object of ascertaining the influence of minute quantities of sulphuric acid on the action of dilute saline solutions on lead. Chemically pure lead foil was cleansed from grease by washing with alcohol and water, and was afterwards rubbed bright on a soft towel. It was cut up into pieces of 12.5 square centimetres in area, each piece was rolled into a hollow cylinder, placed in a flask of about 150 cc capacity, and covered with 100 cc of solution to be examined.

In the case of dilute saline solutions, the addition of 1 grain per gallon of sulphuric acid increased the solvent action of the saline solution on lead to a marked extent.

Hall[231] investigated the action of vegetable acids on lead with a view to ascertaining the effect of preserving fruits etc., in tins. He carried out a large number of experiments with acetic, citric and tartaric acids on lead. Three alloys were made - one containing the two metals lead and tin in equal proportions, another containing excess of lead, and a third excess of tin. Samples of the pure metals exposing the same surfaces as in the alloys were also tested. In the case of acetic acid all the alloys were found to be much less acted upon than the pure metals. As the percentage of tin in the alloy increased, its liability to corrosion decreased.

CHAPTER 8

CORROSION THEORIES

8.1. INTRODUCTION

The science of corrosion had its first period of rapid advancement in the first half of the nineteenth century. This was a result of intense and sustained scientific interest and activity aroused by the invention of the galvanic battery and the controversy over the nature and source of galvanic current.

One of the most significant facts of corrosion, namely that an originally neutral water tends to become alkaline during the corrosion process appears to have been stated for the first time by Austin (232) in 1788, Austin, however, wrongly attributed the alkalinity to the substance which we now call ammonia, and the same mistake was made by Chevallier (233), who repeated Austin's work in 1828.

8.2. ELECTROCHEMICAL THEORY

One of the first announcements of the establishment of a relationship between chemical action and electricity was demonstrated by Nicholson and Carlisle (234). In a paper published in 1801 they stated:-

"We know that when water is placed in a circuit of conductors of electricity, between the two extremities of a pile, if the power is sufficient to oxidate one of the wires of communication, the wire connected with the opposite extremity affords hydrogen gas.

"Since the extrication of hydrogen, in this instance is seen to depend on electricity, it is probable that, in other instances, electricity may also be requisite for its conversion into gas. It would appear, therefore, that in the solution

of a metal, electricity is evolved during the action of the acid upon it; and that the formation of hydrogen gas, even in that case depends on a transition of electricity between the fluid and the metal."

In the same year H. Davy (235) established the intimate connection between the electrical effects and the chemical changes occurring in the battery, and drew the conclusion of the dependence of the one upon the other.

In the following year Wollaston (236) stated that it was probable that, even in the case of decomposition of water by uncoupled metals in acid solution,

"the formation of hydrogen gas depends on a transition of electricity between the fluid and metals,

and that:-

"iron itself has the power of precipitating copper by means, I presume, of electricity evolved during its solution."

Following these announcements in rapid succession, there was a lull for some seventeen years and one of the next comments came in an anonymous letter which was published in Ann. Chim Phys. (237) in 1819 in which it was observed that:-

"iron does not decompose water at ordinary temperature when they are both perfectly pure. But once oxidation has commenced, by whatever cause, it can continue by the action of water alone."

for,

"iron and its oxide should be considered as two heterogeneous bodies of different electrical energy, and capable, by their contact, of effecting the decomposition of water, the same as an element of copper and of zinc in the galvanic pile."

Although this discussion was unsigned, a comment by Hall (238) shortly afterwards, dealing with a different topic, states that Thenard was the author of the paper.

The significance of this paper is that it suggested that rusting was also an electrochemical phenomenon and could well have prompted the investigations of H. Davy which led him to the same conclusions in 1826 when he said;-(78)

"In the rusting of iron, the oxide formed by the contact of moisture becomes the negative surface, and exalts the oxidation of the mass of metallic iron, and consequently extends in circles."

In this work Davy showed that when dissimilar metals dipping into liquid were joined electrically, the corrosion of one was usually promoted, and that of the other depressed, he suggested that copper ships could be protected by a junction with iron or zinc. This was an early example of cathodic protection, more details will be given later.

One of the earliest and most troublesome practical problems in metal decay was that of the corrosion and pitting of copper and brass by saline waters.

H. Davy stated in his historic paper of 1824 (76) in the Philosophical Transactions under the title:-

'On the Corrosion of Copper Sheathing by Sea Water' that it had been:-

"generally supposed that sea-water had little or no action on pure copper, and that the rapid decay of the copper on certain ships was owing to its impurity"

but this opinion could not have been universally held, since patents were taken out by Keir (239) in 1779 and by Collins (240) in 1817, for alloys of copper and zinc adapted to the manufacture of ship sheathing.

In 1807, under an article 'Brass and Copper' the following passages occur:- (241)

Brass is said:-

"to be less subject to rust, and to be acted upon by the vast

variety of substances which corrode copper with so much ease; and again:-

"the principal objects of alloying copper appear to be to render it less liable to tarnish, and especially to be acted upon by common animal or vegetable substances."

In 1822 - that is before the publication of Davy's experiments - a patent was taken out by Mushet, (242) for the manufacture of a metal suitable for sheathings, by alloying copper with very small quantities (2oz to 100 sq. yds) of zinc or tin.

Davy's paper published in 1824 (76) contains an account of an experimental enquiry undertaken at the request of the Commissioners of the Navy Board, and in co-operation with a committee of the Royal Society. This probably represents the first attempt to systematically investigate the causes of the corrosion and to find a remedy for the destructive action of sea-water.

Davy was led to apply the electrochemical theory and observed that copper, which is "only weakly positive in the electro-chemical scale, if only to be rendered slightly negative, the corroding action of sea-water upon it would be nill". Davy's plan of protection consisted of attaching small pieces of zinc or iron to the copper surface; and there is no reason to doubt that so far as the protection of the copper from the attack of sea water was concerned, the plan was entirely successful. It failed however, in practice because the sheathing so protected was found to become quickly loaded with an earthy deposit, upon which sea-weeds and barnacles gathered more abundantly than under ordinary circumstances when protectors were not employed.

The practical consequence of Davy's work was that, although corrosion of the copper sheathing could be readily prevented

by application of cathodic protection, the problem of fouling was not completely solved. On naval vessels a low rate of corrosion of the copper sheathing could be tolerated providing fouling could be prevented; and Davy was able to maintain a balance between corrosion and fouling by varying the area of the protected metal.

The various effects associated with the corrosion and cathodic protection of copper in sea water were demonstrated by Davy in an ingenious manner. A piéce of copper wire several feet in length and wound to form a continuous series of coils was connected to a piece of zinc wire one-half inch in length. The zinc and a portion of the copper were placed in one glass and one coil of copper was placed in each of a series of six other glasses and the circuit was completed. The electrolytic conduction was provided by means of thin wicks. After the current had flowed for some time, the copper coil in each glass was examined. In particular it was noted that in the seventh glass the copper wire was completely covered with the corrosion products of copper.

With the help of Faraday, who was at that time employed by Davy as a laboratory assistant, a series of laboratory experiments were conducted in which pieces of zinc and iron were immersed in sea water. Zinc the size of a pea, or an iron nail, prevented corrosion on 40 to 50 square inches of copper. Encouraged by these results a similar series of tests was conducted in the harbour at Portsmouth. With an area ratio of zinc to copper of from 1:40 to 1:150 no corrosion of the copper occurred, as demonstrated by weight loss measurements. However after exposure for four months, deposits formed on the copper coupled to zinc in areas less than 1:80. These deposits were found by analysis to be composed chiefly of calcium

carbonate, with some magnesium carbonate and magnesium hydroxide. In addition to deposition of these calcareous layers there was considerable fouling by marine organisms. Procedures analogous to those practiced by Davy are carried out in the twentieth century, but these will be discussed in the conclusion to this work.

We are able to gain an insight into Davy's life, work and motivations from a study of his published papers, laboratory note-books held at the Royal Institution and from those who have made a personal study, particularly his contemporaries.(243) He appears to have been interested in the sporting and wider interests of life and have applied this more open and general approach to his scientific study and philosophy, having not just a single hypothesis for each problem which must be defended at all costs.(78)(244)

Up to 1835 developments in tin-plating, and also galvanizing had been by practical innovation rather than by scientific reasoning. No successful attempt had been made to explain in any precise way the fundamentals of the coating, especially the behaviour of the coating when in contact with other metals.

However in that year Edmund Davy published details of some 'recent experiments made with a view to protecting Tin-plate from corrosion in sea-water with some probable applications'(104)

"....If a piece of tin-plate is exposed in sea water for a few days, it will exhibit an incipient oxidation, which will gradually increase; the tin will be preserved at the expense of the iron, which will be corroded. But if a small surface of zinc is attached to a piece of tin-plate and immersed in sea water, both the tin and iron will be preserved, whilst the zinc will be oxidised."

Around 1838 particular interest was being shown by scientists in the protective power of zinc when in contact with other metals, but the correspondence, although primarily concerned with zinc, does illustrate the scientific understanding at the time of the properties of tinned-plate.

A letter from W.T. Brande written on the 26th April, 1838, stated:-(69)

"....In common, tin-plate or tinned iron the combination is such that the oxydizement or corrosion of the iron is accelerated by the tin, so that the iron is the protecting and the tin the protected metal, but in the case before us in which the respective metals are iron and zinc, the reverse ensues, - the iron is here protected and the zinc the protector".

In the discussions that took place on this subject at that time, part of a letter from Professor T. Graham of London University also bears witness to the understanding:-(70)

".... The zinc covering has the advantage over tinning, that, although it may be worn off and the iron below it partially exposed, the iron is still secured from oxydation by the galvanic action, while the smallest quantity of zinc remains upon it.

Whereas tin in common tin-plate affords no protection of this kind, and noting the facts before us, we can have no hesitation in stating our opinion that this method of protecting iron from rust will prove of infinite service and will entirely supersede the employment of tinned iron except in vessels used for culinary purposes, in which we fear, it could not safely be adopted."

From these comments about tinned iron, it is obvious that the contempory scientists of that time, although appreciating the theory of galvanic protection, had failed to reason the benefits of tin as a protective metal when used in canning.

By this time tin had been used as a protective metal in conjunction with iron, in sealed containers, for a period of 15 years.

About this time on the Continent, de la Rive (245) published a notable research in which he showed that impure zinc was more rapidly attacked by acids than the purer form of the metal and attributed the rapid attack to electric currents flowing between the zinc and the impurites.

He was investigating the quality of zinc for use in galvanic piles and became aware of the great difference in the intensity of action of sulphuric acid upon zinc and that this action depended upon the purity of the zinc. He unfortunatly gives no indication of how he first established the relative purities of the metal apart from that of pure zinc, which he obtained by distillation.

He observed that pure zinc was not attacked while commercial zinc was found to liberate large quantities of hydrogen. From this he considered that 'foreign metal' mixed with the pure zinc influenced the rate of decomposition of the water and disengagement of hydrogen and that some form of electro-chemical action had taken place. He investigated this phenomena further, coupling zinc with other metals and established an electrochemical series. He was not able to establish any precise relationship, but shortly afterwards the remarkable series of investigations published by Faraday showed how closely chemical and electrical phenonena were connected. Most of Faraday's electrochemical experiments, although not described as such, were really corrosion experiments, (244) and his formulation of the Laws of Electrochemical Action still serve to correlate the strength of corrosion currents with the rapidity of the destruction which accompanies them.

While Faraday was continuing his investigations in Britain, de la Rive was carrying out further experiments and in 1856 extended his theory to the atmospheric corrosion of metals.(246) These were times of scientific freedom, with information being shared around for the common good irrespective of national boundaries.

Particularly interesting is Faraday's correspondence with the Swiss professor, Schönbein, on the subject of passivity which was published in the Philosophical Magazine.(247)

Instead of the prevailing concept at this time of local galvanic couples being formed between the metal and its oxides, Sturgeon(248) considered that the surfaces of the purest metals are unequal electrically and:-

"The positions of the polar points on the surface will frequently change during the dissolution of the metal on various accounts, depending upon the deposition of oxide formed by the first and subsequent currents, the texture of the metallic points, their polish as they are arrived at during the process, their crystalline structure, and perhaps upon many other causes of still more recondite nature."

In fact both concepts were valid within the context of each investigation.

A further early development in the electrochemical concept of corrosion was that of the differential solution concentration cell proposed by Becquerel in 1827.(249) He showed that a cell may be produced by a single metal and a single fluid of two different concentrations.

R. Mallet utilized this discovery in 1840 to explain localized corrosion of an iron casting which was at the bottom of an harbour at the mouth of a tidal river.(250) He stated:-

"It is well known that the sea water, during the flowing of the tide, from its greater density, forces itself between the

river water like a wedge, and slowly and imperfectly mixes with it, hence two strata, one of fresh or brakish water, the other of salt water below it."

More than forty years later, T. Andrews thought he was the first to discover this cause of corrosion currents, and reported measurements of potential differences developed in tidal streams in 1884 (251) and 1890. (252)

R. Adie in 1847 (253) reported interesting experiments on oxygen concentration cells. He placed two pieces of zinc, or iron, cut side by side from the same sheet, in a running current of water, the one opposed to a rapid part of the current, the other in a still place at the edge. When these were connected with a galvanometer, the piece of metal in the current acted as a 'negative plate'. He stated:- (253)

"With both plates in the still water and a tube filled with oxygen inverted over one, the effect was the same."

Adie continued:-

"It is the greater supply of oxygen to the plate in the current which converts it into a negative.....

"A single plate of iron exposed to water and oxygen gas has local differences on its surface which act in the same way as if the iron had been in two halves and placed in a stream in the manner described....."

The importance of variations in concentration of oxygen and salts in solution in promoting localized corrosion was evident from these experiments, but the significance of these investigations was only partially grasped, and then forgotten. Practical benefit from an understanding of these fundamental environmental factors did not follow until well into the twentieth century. Whereas previously, heterogeneity of the metal, or dissimilar metal contact, was commonly thought to be the important or sole stimulator of corrosion, it now

became widely recognised that heterogeneity of the contacting solution was often the dominant factor.

Although the electrochemical theory of corrosion had been proposed by Wollaston in 1801 and developed by de la Rive in 1830 it was 1903 before it was again revived:- by Whitney.[254] Although Whitney presented no new ideas, his paper was of considerable practical importance. He applied the theory to the corrosion of iron and steel at a time when the cost due to wastage of this major structural material was assuming disturbing proportions. For this reason, his contribution received considerable attention, and was a stimulus to further progress.

Whitney's view maybe summarised as follows:- According to the Nerst theory,[255] iron has a natural tendency to pass into solution in pure water; but it will only dissolve if there is present a second substance in contact with the iron, having a lower 'solution tension' than iron itself. If the hydrion concentration exceeds a certain value i.e. if the solution is sufficiently acid, hydrogen will come streaming from the second (cathodic) substance as a gas; but if the hydrion concentration of the water falls below that value, corrosion will be much slower, since the hydrogen will only slowly diffuse away in solution. In postulating the removal of any appreciable amount of free hydrogen in solution, Whitney made an assumption which is now believed to be wrong.

Hall had demonstrated the necessity of dissolved oxygen for appreciable corrosion of iron in water at ordinary temperatures, yet this fundemental consideration had been overlooked by Whitney. Also Whitney's theory was inconsistent with the knowledge of polarization currents founded upon the work of Helmholtz.[256]

It would have been more correct to say that below a certain

hydrion concentration the production of hydrogen in the free state, at any appreciable quantity, could not occur; only in the presence of a 'depolarizer' capable of destroying hydrogen as it was formed at the cathodic surface would the continuous corrosion of iron from a nearly neutral water become possible; such a depolarizer is oxygen.

An electrochemical theory based on this principle was put forward by Walker and his co-workers (257), who were able to indicate far more distinctly the function of oxygen in the corrosion process. They suggested that the quantity of iron which would dissolve in water in the absence of oxygen was probably limited to the amount necessary to polarize the cathodic portions of the metal. If, however, the water contained oxygen or any oxidizing depolarizer, the hydrogen would be removed continuously from these portions and corrosion would continue indefinitely.

8.3. THE ACID THEORY

Another theory, whose star rose in 1870, shone brilliantly during the latter half of the century and finally dimmed in the early twentieth century, was the Acid Theory.

This theory was often referred to as the 'carbonic acid theory of corrosion'. This however implied that carbonic acid was the only acid which could induce corrosion, and so consequently it finally became known as the Acid Theory. The term carbonic was applied due to the prevalence of carbon dioxide in nature, and the fact that a great deal of corrosion of iron is attributable to its action.

A number of writers (258)(259) attributed this theory to Crum Brown (260), and refer to his classical paper read before the Iron and Steel Institute in 1888. In this paper, however, Brown never claims to be the instigator. It was in fact an

expression of the generally accepted theory of the day, and was not new in itself. No fewer than eighteen years previously, in 1870, Calvert performed a number of experiments from which he concluded that an acid (carbonic acid) was essential to corrosion. The explanation of the theory based upon the experiments of Calvert (261)(262) is as follows:-

Clean blades of iron and steel were introduced into a series of tubes and placed over mercury, together with various gases. After four months the tubes were examined and the results appeared to show that in the absence of carbon dioxide no corrosion took place. No particulers were given as to the temperature and the extent of saturation of the moist gases by water vapour, so that it was impossible to say if liquid water ever condensed upon the metal.

Calvert's experiments were rather inconclusive, although it appears that for many years this was not realised.

In 1881 Brown (260.), summarised briefly the most important facts then known on the corrosion of iron, and supported the idea that the action was primarily the result of acid attack - the acid usually being carbonic.

It was considered that iron was converted into rust through the combined action of the oxygen and carbonic acid of the air in the presence of liquid water, the carbonate or bicarbonate of iron (ferrous), first formed being gradually converted by the further action of atmospheric oxygen into ferric hydroxide or rust. The successive changes were summarised by Brown in the following equations:-

$$4(Fe + H_2O + CO_2) = 4\,FeCO_3 + 4H_2$$

$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2$$

The action of alkalis preventing the rusting of iron was explained by their power of absorbing carbonic acid, without

which rusting was supposed to be unable to occur.

Dunstan et. al.[263] on conducting a series of experiments for the purpose of explaining the rapid corrosion of iron and lead pipes by soft water came to the conclusion that the nature of chemical change involved in the atmospheric oxidation of metals was not fully explained by this theory and continued further investigations. This led them to develop what became known as the 'Hydrogen Peroxide Theory'.

8.4. HYDROGEN PEROXIDE THEORY

Dunstan et. al. considered after considerable investigation that Whitney[254] had been correct in assuming that pure oxygen and liquid alone were essential to the corrosion of iron, the presence of an acid being unnecessary. Their interpretation of this conclusion was however entirely different. They considered that hydrogen peroxide was formed as an intermediate product during the formation of rust.

The sequence they suggested can be analysed as follows:-

$$2Fe + 2H_2O = 2FeO + 4H$$

$$\downarrow$$

$$4H + 2O_2 = 2H_2O_2$$

In the first stages, two molecules of peroxide are formed during the oxidation of two atoms of iron to ferrous oxide. However only one of the H_2O_2 molecules is required to oxidize the two molecules of FeO to rust.

$$2Fe + H_2O_2 = Fe_2O_2(OH)_2$$

The excess of hydrogen peroxide attacking any uncorroded iron yielding ferrous oxide and rust

$$Fe + H_2O_2 = FeO + H_2O$$

$$2Fe + H_2O_2 = Fe_2O_2(OH)_2$$

"rust

Dunstan et al. gave no details of their H_2O_2 detection techniques. The presence of H_2O_2 would decolourise a solution containing a few drops of potassium permanganate whereas oxygen would not.

The following observations were made by Dunstan and his co-workers on the following metals.(263)

Copper:- After forty-eight hours the liquid was of a faint blue colour, and gave a distinct reaction for hydrogen peroxide.

Mercury:- After two hours a distinct reaction for hydrogen peroxide was found.

Silver:- After twenty-four hours a trace of hydrogen peroxide was found.

Lead:- The liquid became milky at once and gave a reaction for hydrogen peroxide.

Tin:- The reaction for hydrogen peroxide was not very clear.

Zinc:- A well marked reaction for hydrogen peroxide.

Iron:- Although examined from time to time, no hydrogen peroxide could be detected.

It can be noted that hydrogen peroxide could be detected in the case of all metals except iron. Dunstan argued that because iron was decomposed very quickly its presence was difficult to detect. Unfortunately Dunstan did not give very much experimental information.

Moody(264) however showed that pure, neutral hydrogen peroxide in dilute solution had no visible action upon iron, although it is itself catalytically decomposed by the metal if in a finely divided state. This opposed the results obtained by Dunstan, and can possibly be attributed to the fact that his hydrogen peroxide was not perfectly pure, resulting in the second group of equations representing the corrosion of iron by the action of hydrogen

peroxide alone to be incorrect.

Also according to this theory the power of caustic soda and chromic acid to inhibit corrosion is attributable to their tendency to decompose hydrogen peroxide and so remove it from the sphere of action; but other workers (264a) have found that other substances such as potassium iodide, which removes hydrogen peroxide, do not inhibit the rusting of iron.

It is also not necessarily the case that because chromic acid and the alkalies destroy hydrogen peroxide that they must necessarily prevent its formation.

The hydrogen peroxide theory failed to receive any appreciable support, but probably served to highlight attention on other theories that were then supported.

In correspondence with Dr. T.P. Hoar, (Reader in Material Science at Cambridge University and a specialist on corrosion,) he mentioned that he knew one of the authors of the 'Hydrogen Peroxide' paper, during his retirement. He never heard him speak of this particular paper and it appears that the peroxide theory was largely an hypothesis rather than a theory.

There is no doubt that peroxide is sometimes produced during corrosion processes, and in other processes where oxygen is involved. However it does not seem to be a particularly important intermediate in corrosion matters.

The controversy continues but current investigators consider that in most corrosion systems an electrochemical theory prevails.

8.5. SHERARDIZING

The general theory given by the inventor, Cowper-Coles (98) known as the 'Vapour Theory' was not challenged for several years. A principal reason for this was the subsequent lack of research for some time by other workers.

In this theory he considered that the vapour of zinc is the active agent in the deposition of the coating. The zinc vapour present being sufficient to allow enough zinc to be condensed on the iron to form the protective alloy. Although the vapour pressure of zinc at sherardizing temperatures is almost negligible, that of the finely divided zinc or blue dust is several times greater. That this is the cause of the relatively higher rate of deposition than could be obtained from ordinary zinc is the basis of the vapour theory. In the early days of the process, the only factors controlled were the temperature and the time of operation, and it was expected that a batch of zinc dust could be used without addition until exhausted of metallic zinc. On account of the volume of dust at disposal diminishing, the practice arose of adding new dust after each operation to maintain the stock. Most careful attempts were made to maintain perfectly uniform temperatures but this was not always possible and bad work resulted.

Systematic scientific experiments were carried out and established the fact that if the percentage of metallic zinc in the dust was kept constant similar results were always obtained between the same temperature limits, and these limits were much wider than expected.

This led to Hinchley's (265) proposal of the "Contact Theory". He considered that a film of iron oxide is first produced upon the surface of the article which was reduced by the zinc, in contact, to metallic iron which alloys with the excess of zinc present to form a film replacing exactly the oxide film previously formed.

However Storey (266) later pointed out, that he found that sherardizing could be carried out more easily in a vacuum where the oxide is not formed and under these conditions

the 'Contact Theory' did not hold.

Much later in 1924 Mc Culloch (267) investigated how temperature variations effected the iron content of the coating. There are many variables involved with sherardizing such as temperature, time, concentration of zinc-dust in inert powder and the size of zinc particles. Consequently it is unlikely that one acceptable theory will be found that covers all these eventualities.

CHAPTER 9

TIN-PLATING

9.1. EMPIRICAL WORKING (CIRCA 1800 - 1835)

9.1.1. Introduction

By the beginning of the nineteenth century the process of tin-plating was well established in Britain, with more tin-plate produced here than in any other country. This was primarily due to the presence of tin ores and to the rolling process developed by Hanbury at Pontypool.
There were a number of important features that appeared to govern the location of a plant. The localisation of the industry could be considered from two aspects:- the competition of large areas for the industry, and the competition of various spots within the general area for works sites. The general area itself was determined by natural facilities which fall into three groups:-

1) The presence of power in the form of coal or water supply.

2) The cost of assembling the raw materials, tin and iron.

3) The cost of distributing the finished product. (good port facilities)

The suitability of South Wales had been obvious. There appears to have been one factor of paramount importance and this was the presence of the iron industry. The tin-plate industry was primarily established to relieve the depressed condition of the iron trade at that time. The presence of water was required for technical operations such as cleaning the plate after pickling and for driving the

water wheels. It was a combination of these features, therefore, which would increase the attractiveness of an area for possible development and not the size of a town or local market for the goods.(268)

Although these factors influence the choice of a site, after a time other considerations have to be taken into account which could cause the original site to be closed or any expansions to be carried out in another area.

In the second half of the nineteenth century steel replaced iron sheet. Gradually at this time local ore became exhausted and foreign importations began in South Wales. All new steel works were accordingly built near the coast to avoid expensive inland rail transport.

9.1.2. Early developments

The process had been developed to produce blackplate and through this process the industry was able to make tin-plate more cheaply than its Continental rivals.(63)

At the beginning of the century there were eleven mills operating in Britain, mostly in South Wales and Monmouthshire. Each rolling-unit consisted essentially of two stands of 2ft. high rolls. Roughing was carried out on one stand and finishing on the other, which had more carefully finished roll-surfaces. The unit also comprised shears and two or more reheating furnaces.

The starting point was a sheet bar about 8 inches wide and $\frac{1}{2}$ inch thick, the length being sufficient to make the desired sheet width with an allowance for trimming. The weight varied from about 18 to 80lb. Two such bars were taken from the furnace, where they had been heated to about 790°C in a

smoky reducing flame. With a man on each side of the rolls, one bar was fed with tongs by the roller into the roll-bite, to be returned over the top by the catcher while the second bar was fed in. After several rapid passes the bars had elongated along their original 8 inch dimension to form approximately square sheets. The two were then 'matched', that is placed together, reheated, and rolled as a pair until the thickness was reduced to about half. The sheets were then separated, each doubled along its centre, matched again, and rolled in 'fours'. The process continued, the folds being sheared off and the sheets separated from time to time to prevent permanent sticking, and to bring individual sheets in turn to the outside. Finally, rolling was completed in 'eights'.(63) Sometimes the sheets were separated with iron knives, cold rolled to get the surface smooth; pickled in vitriol to remove the black spots on the sheets, and to prepare it to receive the coating of tin.(268) The black pickled sheets were then taken to a pot containing tin and palm oil. The purpose of the palm oil was to improve the 'flow' properties of the tin and enable a better finish to be obtained. After the sheets had been passed between the rollers coated with tin, a washman brushed off any surplus tin and put them into bran. They were then dusted by girls, and taken to assorters, who sorted out the best plates. They were then put in boxes, weighed and branded as 'best sheets', the others as waster sheets, the prime ones at that time being sold about two shillings a box more than the wasters.

In 1805 the British industry had an annual production of 80,000 boxes (about 4000 tons) of which 50,000 boxes (about 2500 tons) were exported.(63)

The pattern in trade, location, and organization for the British industry had now been set for many years ahead.

9.1.3. Europe's meagre challenge

The successful establishment of tin-plate manufacture in Great Britain was in striking contrast with the history of the industry in other European countries.

The German industry had declined partly through technical obsolescence.

In France tin-plate production had been abandoned during the Revolutionary period and was making very slow progress in redeveloping.

Works set up in the Netherlands, Russia, Spain, and Sweden were able to continue in production for only a limited period. Tin-plate making was abandoned in Sweden early in the century, but it continued to be carried on in Germany and Austria. However all these industries were small and none of them produced enough to meet the domestic demand of the countries concerned. This demand was mainly for dining utensils and ornaments.(263)

As the Continental industry stagnated or slowly expanded, production in the British industry provided a complete contrast. Between 1800 and 1891 it grew rapidly and the output expanded nearly one hundred and fifty times. Though in Britain demand increased, the main stimulus for the expansion came from the growth of overseas demand, particularly the creation of new uses of tin-plate for canning food.

9.1.4. The Worshipful Company of Tin-plate Workers

Far from the hard and rugged world of tin-plate manufacture on some bleak Welsh hillside, there existed in London a company of men who were very closely associated with tin-plate. They were the Worshipful Company of Tin-plate Workers of the City of London. In the year 1800 there is a record that these gentlemen,(66) "had a dinner provided on the Lord Mayor's Day for 36 Liverymen at 3 p.m., and a supper in the evening, but tea was to be dispensed with." The company had been formed in the seventeenth century as a breakaway Company from the 'Ironmongers'. The general supervisions and regulations of the trade in and around London came into the hands of the new Company.

The Company had only slender resources and depended on the subscriptions of its Members. It progressed through the century with varying fortunes. The reason these men came together was partly social and partly because of their associations with the trade. They could discuss matters of mutual interest in a convivial atmosphere.

Fig. 53 is an illustration of the Freeman's Oath, and Fig. 52 shows the Coat of Arms of the company.

9.1.5. Early development of tin-cans

9.1.5.1. Introduction

An event of significance in the development of the tin-plate industry, which occurred in the early nineteenth century, was the application of the plate to preserve foods in the form of tin-cans.

The art of preservation in glass jars was first developed by a Frenchman, Nicholas Appert. (SEE 269)

The term 'canning' appears to have originated in America around 1874 where the process using tinned iron was first automated.

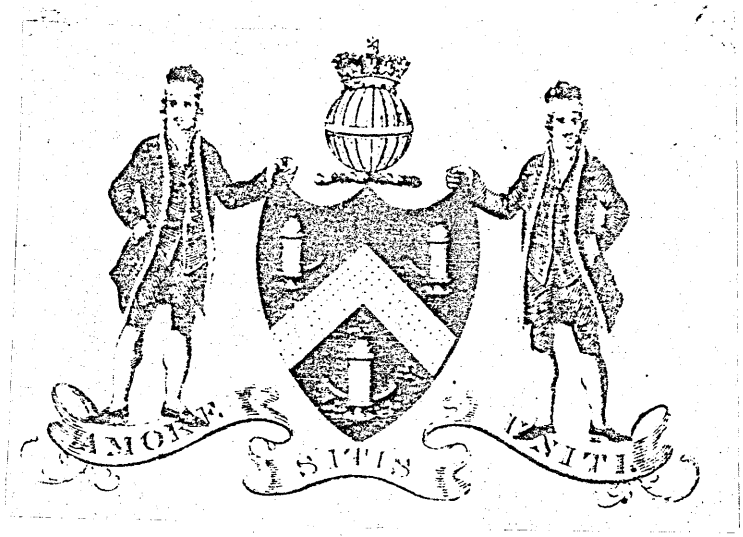


Fig. 52 COAT OF ARMS OF THE WORSHIPFUL COMPANY OF TIN-PLATE WORKERS OF THE CITY OF LONDON (66)

YOU ſhall ſwear that you will be good and true to our Soveraign Lord the King's Majeſty, that now is, and to his Heirs and Succeſſors, Kings and Queens of this Realm, and in all things lawful and reaſonable relating to the ſaid Company, according to your Power, ſhall be obedient to the juſt and lawful Orders and Conſtitutions of the Maſter, Wardens, Aſſiſtants and Governours of this Company for the time being, and their Succeſſors, and ſhall readily appear upon all Summons by their Beadle or other Officer, Except you have ſufficient cauſe to be abſent, or elſe you ſhall pay all ſuch Sums, Penalties and Fines as you ſhall forfeit, according to the lawful Ordinances of this Company for breaking the ſame. All the lawful Acts, Ordinances and Orders made for the good Rule and Governance of the ſaid Company, You ſhall to your power obſerve and keep, or elſe pay ſuch Penalties and Fines, as you ſhall according to the ſaid Ordinances forfeit, by reaſon of your diſobedience or breaking of the ſame. All this you ſhall faithfully do and perform to the utmoſt of your power, and as far as lawfully you may.

So help you GOD and the Holy Contents of this Book.

Fig. 53 THE WORSHIPFUL COMPANY OF TIN-PLATE WORKERS. THE FREEMAN'S OATH. (66)

Tin-plate for canning appeared on the scene for the first time in a British patent granted in 1810 to P. Durand, of (269a) Hoxton Square, Middlesex. The patent mentions:-
"....an invention communicated to him by a certain foreigner residing abroad". In the description however only a passing mention of tin was recorded amongst a list of "other metals and fit materials".
The mention in the patent of "....a certain foreigner residing abroad" could well have been Nicolas Appert, a Frenchman, who in the same year 1810 published a book on preserving Animal and Vegetable substances for many years (272) (SEE REF 269)
Although Durand and also de Heine had patented the use of tin and iron containers respectively for preserving foods neither of them engaged in canning on a commercial scale.

9.1.5.2. First commercial successes

In the following year a process was developed in England by John Hall of Dartford, and his associate Bryan Donkin, which produced the first canned foods in tin-plate, which were actually marketed.
In a history of the firm of J. and E. Hall Ltd., it is (269) stated that John Hall and his associates paid £1000 for "a friend's Patent by a chemist named Appert".
After several years experimenting with preserving foods Donkin and Hall opened a factory in Blue Anchor Road, Bermondsey, supplying tinned foods for the Navy. At this time most of Europe was at war and Britain was maintaining a large naval force at positions all over the world. Many sailors were sick from scurvy and the development of the preserved food processes was a godsend to them.
In 1817 Donkin and Hall produced a brochure which contained testimonials from prominent people testifying to the quality

of the preserved foods. Among the testimonials was one from Sir Joseph Banks, then President of the Royal Society, sent in 1814:-

"I know of no objection to my name being placed among the very respectable names which are printed in your Prospectus, as giving their testimony in favour of the nutritious qualities of your embalmed Provisions".

During the 1820's canned foods had become a recognised article of commerce in Britain and in France and it was not long before the industry spread to America where it was to become by far the greatest canning industry of all.(269)

9.1.6. Parkes' detailed account of the process

Apart from the development of canning as a specialist part of the tin-plate industry, the production of tin-plate for many miscellaneous trades continued.

A descriptive account of the process pursued in the manufacture of tin-plate at this time can be found in a letter sent by Samuel Parkes to B. Naylor in 1818.(68) Unfortunately Parkes' gave little diagrammatic representation of the process. However, his description is a detailed record of the process in the early nineteenth century.

The first operation was to manufacture the plate prior to tinning.

Bar iron was first rolled into plates of the requisite thickness and cut by hand shear to sizes suitable for various applications.

The scaler then took them and bent ends across the middle into the form of a 'Vee' and then 'scaled' the plates in a furnace or oven. The plates were then cleansed by steeping

them for four or five minutes in a mixture of muriatic acid and water in the proportion of four pounds of acid to three gallons of water. This was followed by heating in a furnace until they were 'red hot' and the scale had been removed by the heat.

After cooling and beating smooth, the plates were rolled a second time between a pair of hardened cast iron rollers, and placed individually in troughs filled with a solution called 'The lees'. This was water in which bran had been steeped for about ten days until it had acquired sufficient acidity for the purpose. After remaining in this liquid for about ten hours they were steeped in a lead trough containing a mixture of sulphuric acid and water and agitated for about an hour to acquire a bright surface free from black spots. This is a process which became known as pickling. They were then put in pure water and scoured with hemp and sand, followed by a further dipping in fresh water.

The process mentioned so far constituted the surface preparation. Analysing the process it would appear that there would be two key operations requiring particular skills and judgement. The first one would be that performed by the furnace operator since he would need to judge the correct length of time for all the scale to be removed. The amount of scale on each plate would naturally vary, depending upon the conditions under which the plates had been stored prior to this process. A plate on the top of a pile, probably left uncovered, would be more corroded than one in the centre and it is doubtful whether the processes carried out prior to that of heating in the furnace would have eliminated these discrepancies.

The other operation requiring particular skill would be that of 'pickling', since any plates left too long in the acid would become stained and blistered and would be unsuitable for plating. Consequently considerable skill and judgement would be required, and a person particularly skilled in this could probably command a high wage. Comparing these two operations; although pickling would be more critical and the working conditions in acidic fumes more injurious, the furnace man would have more problems viewing the operation, stage by stage, because of the greater intense heat than the pickler would have. Consequently a greater experience would be probably required by the furnaceman.

In the tinning process, the sheets were first dipped in a pot containing just hot grease. The purpose of the grease probably was to increase the 'flow' properties of the tin. They were then removed with the grease still adhering to them and stacked vertically in a pot containing hot tin and grease. The grease in this instance also helped to prevent the oxidation of the tin. Three hundred and thirty eight plates were usually put into this pot at once and they usually remained in it for $1\frac{1}{2}$ hours.

After draining and cooling the plates were put in a 'list pot'. This was a vessel containing a very small quantity of melted tin. After this second coating of tin the plates were cleaned of tallow using bran and after drying were put into boxes.

Fig. 54 shows a diagrammatic representation of the tin-plating process as described in the Parkes' letter.

Fig. 55 and 56 give details and prices of tin-plate during September 1817 in London.(63)

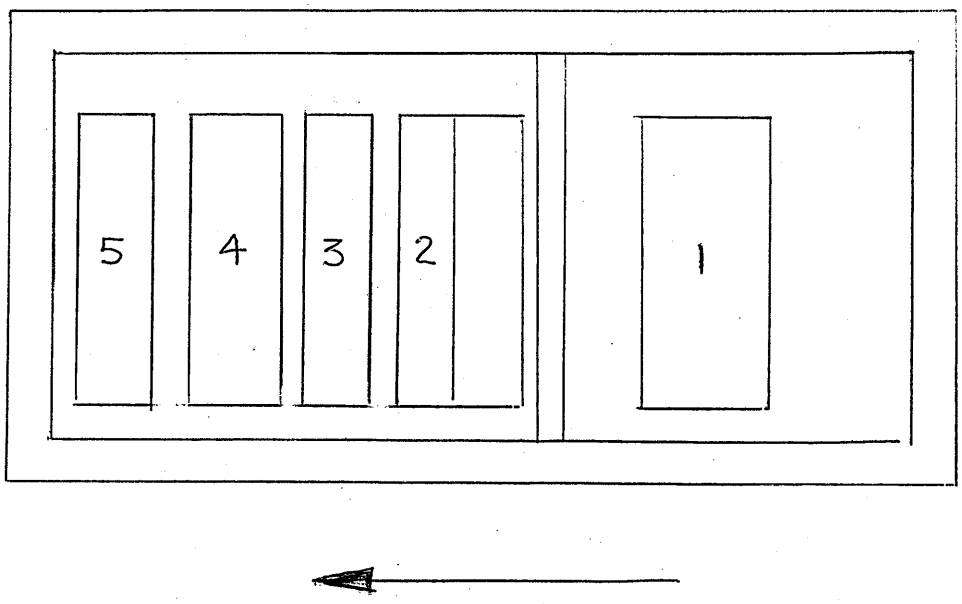


Fig. 54 DIAGR. REPRESENTATION OF TIN-PLATING IN THE EARLY NINETEENTH CENTURY, AS DESCRIBED IN A LETTER FROM S. PARKES TO B. NAYLOR ON THE 20th FEB. 1818 (68)

1 - TIN POT

2 - WASH POT CONTAINING A "PARTING"

3 - GREASE POT

4 - PAN CONTAINING GRATING AT BASE FOR DRAINING

5 - LIST POT

Names.	Sizes.	No. in a Box.	Weight of each Box.	Marks put on the Boxes.
	inches.		c. q. lbs.	
Common No. 1	13¾ × 10	225	1 0 0	CI.
„ „ 2	13¼ × 9¾	„	3 21	CII.
„ „ 3	12¾ × 9½	„	3 16	CIII.
Cross „ 1	13¾ × 10	„	1 1 0	XI.
Two Cross „ 1	„ „	„	1 1 21	XXI.
Three „ „ 1	„ „	„	1 2 14	XXXI.
Four „ „ 1	„ „	„	1 3 7	XXXXI.
Common Doubles	16¾ × 12½	100	3 21	CD.
Cross Doubles	„ „	„	1 0 14	XD.
Two Cross Doubles . . .	„ „	„	1 1 7	XXD.
Three „ „ . . .	„ „	„	1 2 0	XXXD.
Four „ „ . . .	„ „	„	1 2 21	XXXXD.
Common Small Doubles . . .	15 × 11	200	1 2 0	CSD.
Cross „ „ . . .	„ „	„	1 2 21	XSD.
Two Cross „ „ . . .	„ „	„	1 3 14	XXSD.
Three „ „ „ . . .	„ „	„	2 0 7	XXXSD.
Four „ „ „ . . .	„ „	„	2 1 0	XXXXSD.
Wasters Common No. 1 . .	13¾ × 10	225	1 0 0	WCI.
„ Cross „ . .	13¾ × 10	..	1 1 0	WXI.

Fig. 55 DETAILS OF TIN-PLATE MANUFACTURED IN THE EARLY NINETEENTH (63) CENTURY.

Sorts.	Weight.	Prices per Box.	No. in each Box.
	lbs.	s.	
C No. 1 . . .	112 to 115	41	225
C „ 2 . . .	103 „ 106	39	
C „ 3 . . .	98 „ 101	37	
X „ 1 . . .	140 „ 142	49	
XX „ 1 . . .	160 „ 163	55	
XXX „ 1 . . .	182 „ 185	61	
CD	98 „ 103	37	100
XD	126 „ 129	45	
XXD	147 „ 150	51	
XXXD	168 „ 171	57	
CSD	167 „ 170	63	200
XSD	188 „ 191	69	
XXSD	209 „ 212	75	
Wasters CI . . .	112 „ 115	35	225
„ XI . . .	140 „ 143	43	

Fig. 56 A LIST OF WHOLESALE PRICES OF TIN-PLATE IN SEPTEMBER 1817 (LONDON)(63)

9.2. WELSH INDUSTRIAL SUPREMACY (CIRCA 1835 - 1891)

9.2.1. Development of the tin-can

In 1841 a great improvement occurred in the methods of processing foods.

Stephen Goldner patented:- (270)

"A mode of heating the vessels in which animal or vegtable substances are to be preserved by driving off the atmospheric air and producing a vacuum therein, which has heretofore for the most part been performed by stoves or ovens which is liable to burn the materials.

I employ a chemical bath in the manner described by John Wertheiner's Patent. (271) I use a solution of muriate of lime or nitrate of soda, but prefer the former because I am enabled to obtain a constant temperature of 270° - 280° F without much evaporation".

This method of preserving the food proved to be very beneficial in both the quality of the food preserved and its can - life. It was also much cheaper.

At this time attention began to be concentrated on the methods of canning, and the problems associated with each new commodity that canners handled. Corn on the cob, peas, salmon, oysters, sardines and milk were but a few of the foodstuffs already available in cans by the mid nineteenth century. (270)

Goldner, who had patented the new processing method in 1841, was not long in getting himself accepted as a contractor for the Admiralty. The next important development came in the mechanisation of can making. (272) This was brought about by the invention of the drop-press by Taylor, an American, during 1847.

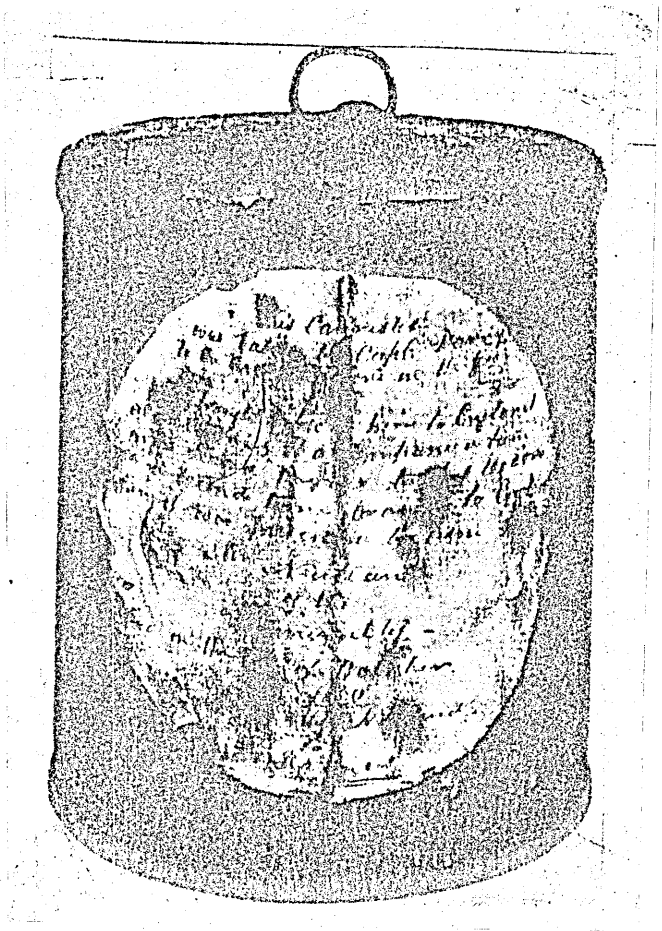


Fig. 57 A TIN-PLATE CAN, CONTAINING ROAST VEAL, OPENED IN 1938 AFTER BEING SEALED FOR 114 YEARS (272)

This machine converted flat discs into the vertically flanged caps for the can ends by dropping a heavy die on to them. Two years later in 1849 a fellow countryman, Henry Evans, devised a pendulum press for the same purpose, and within a year or two improvements were effected which resulted in the first 'combination' press. This cut out the discs from the flat sheet, flanged them ready for capping the body, and in the same operation punched out the filler holes. Unfortunately none of these devices appears to be still in existence.

About 1849 serious reports of faulty tins and bad meat were continually coming from the Admiralty and matters went from bad to worse. Meat was condemned in large quantities and consequently it became necessary for a Government Select Committee to be appointed.(272) After exhaustive enquiries the Committee concluded that the chief cause of the canned meat going bad was a failure to ensure the complete expulsion of air from the canister and inadequate cooking of the contents. For a considerable time after this, canned meat was treated with suspicion.(273)

9.2.1.1. Improvements in the opening techniques

The operation of opening a can was up to this period regarded as both difficult and dangerous. There was a comparative lack of uniformity in the thickness of the tin-plate, and the tinsmiths could not work with the precision developed later by machines. This difficulty of opening cans was a serious deterrent to the housewife, and consequently inventors turned their attention to devising cans which could be opened easily.

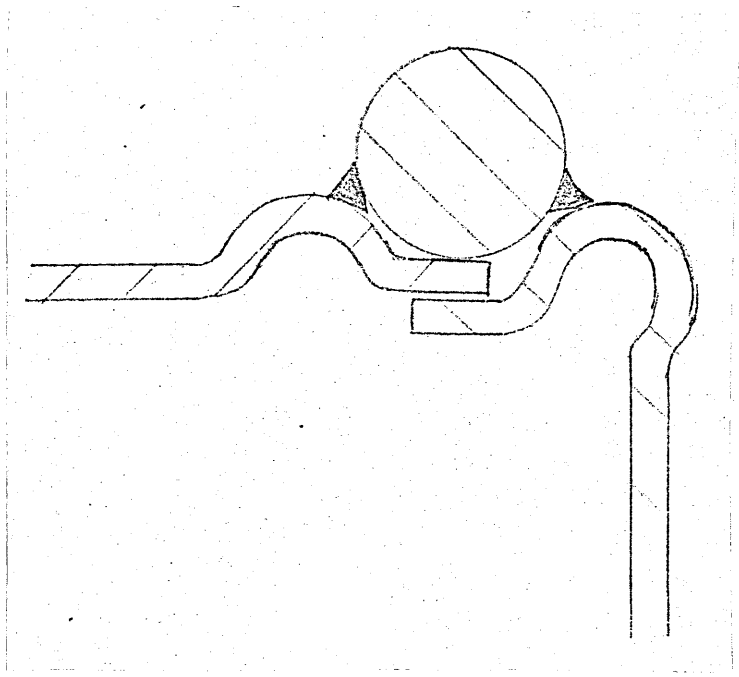
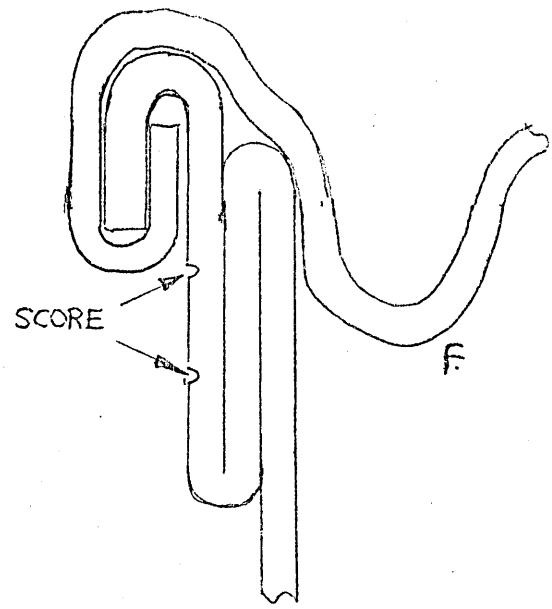


Fig. 58 BOUVET'S SELF-OPENING CAN INCORPORATED IN BRITISH PAT., 1862/2569 (274)



(277)

FIG 59 WIDGERY'S SELF OPENING SARDINE CAN

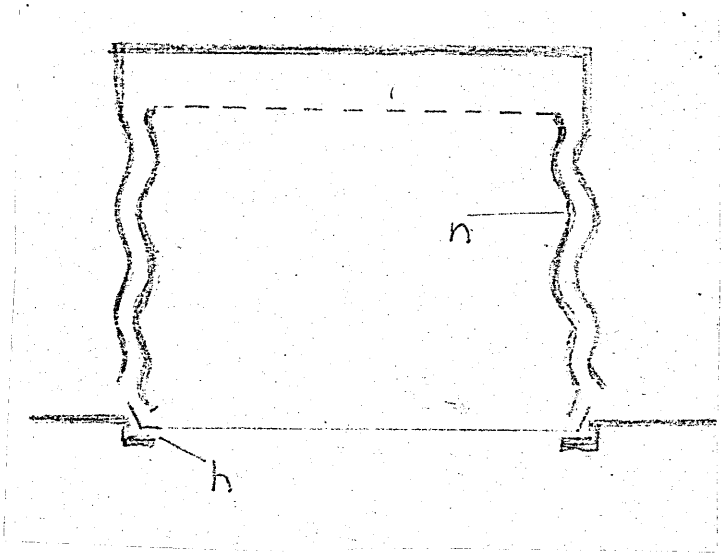


Fig. 60 DEVOE'S "TAGGER TOP" CAN INCORPORATED IN BRITISH PAT., 1868/1809 (275)

The first important development of this kind was due to J. Bouvet in 1862.[274] A wire was laid and soldered in the groove formed between a corrugation near the edge of the lid and a bead at the top of the can body, (fig. 58.) One end of the wire was carried up out of the groove and lightly soldered at its end to the middle of the lid, so that it could be pulled up easily and then ripped out of the groove. The lid was then unattached to the body and could be lifted out.

Another class of easily opened tin-plate can, which was hermetically sealed by soldering, was known as the 'tagger top' can. In these the hermetic closure is a sheet of very thin tin-plate, protected by a strong cover from mechanical injury. The cutting away of the 'tagger top' was easy and the loose cover then served as a lid for the opened container. The first authentic 'tagger top' was due to F.E. Devoe in 1868. He devised it to exclude air from paint cans. The cans were closed by a fixed cover with a hole, h, in it, over which was soldered the nozzle, n, closed below by a thin sheet of tin-plate, (fig. 60). To open the can the screw cap was removed and the thin sheet of tin-plate cut out with a knife.

Five years later W.H.I. Howe,[276] of New York, obtained a British patent for tagger topped preserve cans in conjunction with a loose cover for use after destruction of the 'tagger' which, he said, may be made of tin foil.

Fig. 59 illustrates the details of a sardine can patented by Widgery in 1871.[277] The ends are attached by the method of double seaming to the body, which has a flattened S shaped

double fold near the top. The outermost of the three thicknesses of tin-plate at the double fold is deeply scored for the whole length of its circumference in two parallel lines. The side seam is lap - soldered and a projecting tongue is left between the scoring lines at the lap seam. The bottom of the can has a recess portion which houses a key, which is attached to it by a spot of solder, and is nearly severed by a cut just clear of the solder. To open the can, the key is broken away from its soldered extremity, the tongue at the side seam is threaded through it, and the key is then rotated so as to wind off completely the weakened strip between the scored lines. The lid is then freed from the body and can be replaced, It is retained in position after opening by the flange, f, in the lid. The edges of the can and lid are perfectly safe.

9.2.1.2. Internal lacquering introduced

The internal corrosion of cans caused Peltier and Paillard of Paris in 1868 to try and prevent the trouble by varnishing the insides of cans. They used a varnish of gum copal, linseed oil, and turpentine.(272)

Fourteen years later Parry and Cobley proposed to make cans from tin-plates coated with sodium or potassium silicate. After drying the plates, they were to be washed in a dilute acid.

9.2.2. Industry's growth in South Wales

During the period when the industry catered for the trades which produced durable consumer goods, its growth remained slow; but when the use of tin-plate for canning food and petrol developed, it expanded more rapidly. This development favoured the South Wales section of the industry rather than the Midland section. The number of works in South Wales more than

trebled from 25 existing in 1850 to 90 in 1891,[278] whereas the total of works outside South Wales had only increased by three. The Midlands produced mainly heavily coated plates for durable purposes; the Welsh industry produced lightly coated expendable plates for food and petrol canning. While the market for the product of the Welsh industry grew, that for the Midland plate declined. A second factor hastened this process, this was the replacement of iron by steel. As the Midland iron industry lost ground, the tin-plate industry there found it impossible to compete with the Welsh industry, so that tin-plate manufacture became even more localized in South Wales.

Within South Wales, the second half of the century saw a shift in the centre of gravity of the industry. Until about 1850 the Eastern area was the more important, but from that date the main centre of tin-plate production moved to the Western area, the coastal belt between Port Talbot and Carmarthen.

Fig. 61 shows the tin-plate works at Kidwelli in Carmarthenshire with a claim to be the oldest in the country. A plaque let into the wall above the door makes this claim.

In this area there grew up a number of 'tin-plate towns', which were largely dependent on the industry for employment. The first tin-plate works in Llanelli is recorded as having been built in 1846 at the Dafen Works.[279] By 1886 there were six tin-plate works in the town, and at this time forty one of the works in South Wales were West of Port Talbot.

The typical tin-plate works remained small, the majority having three or four mills. As there were no radical changes in the technique which permitted any appreciable economies of scale, and the demand did not yet exist for a standardized

Fig. 61 THE PLAQUE LET INTO THE WALL ABOVE THE DOOR AT THE KIDWELLY WORKS READ :

THESE
TIN WORKS ARE
THE OLDEST IN THE KINGDOM
WERE REBUILT
BY HASEWOOD
HATHAWAY AND PERKINS
ANNO DOM: 1801

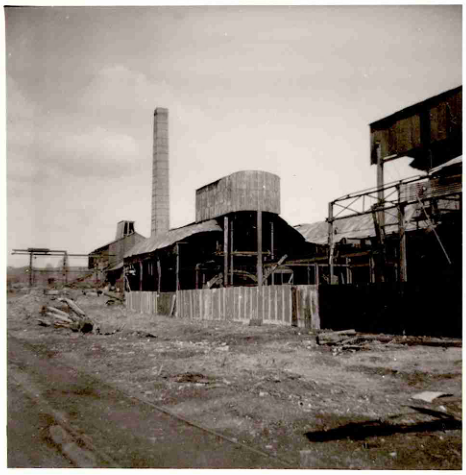


Fig. 61 (a) -THE KIDWELLY TIN-PLATE WORKS (1973)

product, there were no economic advantages to be secured by building larger works. The largest mill in Llanelli was owned by E. Morewood.

9.2.3. Morewood's major contribution to process mechanisation

Morewood made a major contribution to the industry by developing, along with Rogers, rolls in the tin pot. It was at this juncture that the development of tin-plating and galvanizing became the most closely related, since it was from Morewood's rolls that the first rolls for galvanizing were developed. Full details of this are given later in Chapter 10.

Tinning had been accomplished by hand, the sheet being literally dipped into a pot of molten tin, and then into a pot of hot palm oil; then thrown into a box of bran and polished by hand. The resultant tin-plate was a very poor article, with considerable variation in the thickness of coating. It was also likely to show tong marks and other imperfections.

The first of Morewood's and Rogers' patent specifications was made in 1843, and a second one in 1846.(280)(281) They employed a tin pot with a secondary pot containing palm oil, the secondary pot being at a considerably higher level. In the oil pot were arranged four pairs of rolls, each in a horizontal place and arranged vertically, one pair above the other. The plate was pushed by the dipper, edge down, through the molten tin until the edge struck hoops on a lever in the bottom. The lever then lifted until the plate engaged the bottom pair of rolls in the oil pot. The plate then passed successively through all four pairs of rolls. The plate

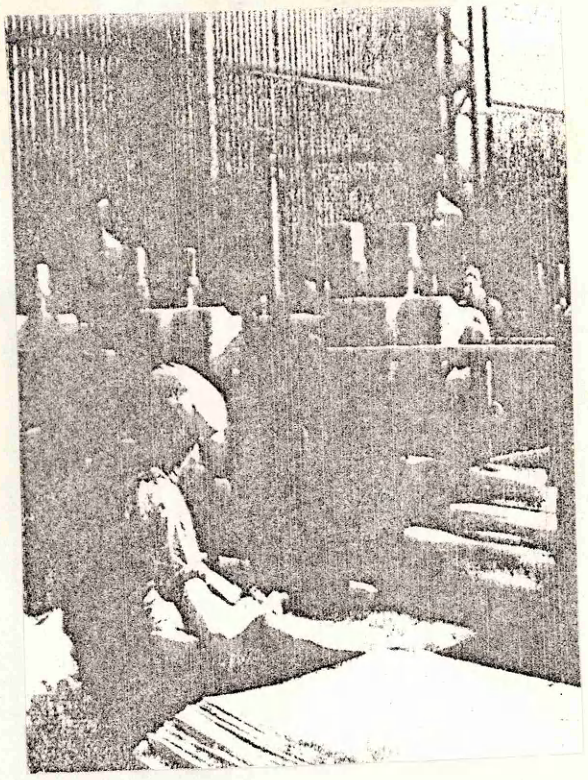


Fig. 62 WORKMAN OPERATING THE COLD ROLLER (286)

had a better finish, a uniform coating, and the surplus tin was squeezed off and drained back into the tin pot. The branning was done as in the old process.

Several minor improvements, mainly in branning, were made from time to time, but the next radical improvement was the introduction of the Lydney duplex pot, first utilized by the firm of Thomas and Co., Lydney, Gloucestershire.

In this invention two pots were used, one containing tin and one containing palm oil. They were placed one behind the other, and curved guides were used. The plate passed through the tin pot, which had one pair of rolls, and onto the oil pot, having three pairs of rolls arranged substantially as in the Morewood pot. This enabled the speed of production to be more than doubled. (2819)

9.2.4. Introduction of the steel base

One of the greatest developments of all in the tin-plate industry, during the second half of the nineteenth century, was the introduction of steel in place of wrought iron for the base plate. The first steel-based tin-plates were made about 1856, due to the collaboration between Sir Henry Bessemer and Phillips and Smith of Llanelly, but the business did not progress favourably.

Later in 1864 experiments were made upon Dowlais bars by Joshua Williams of Aberdulair Works. The first intention was to compete with charcoal iron, but the attempt had to be abandoned. The bars would vary in softness within their own length, they were not homogeneous, and the material was too hard for the fragile machinery then in use. (2852)

These endeavours to compete with high priced charcoal iron having failed, competition ceased until Bessemer bar prices were reduced so that they could be used as a substitute

for puddled bar iron.

Bessemer steel had been developed originally for rails, but it was used only when Bessemer makers decided to look out for new markets, and it was not fully introduced into the tin-plate trade in South Wales until 1881.(283)

The true beginning of the manufacture of steel for tin-plate was attributed to Sir William Siemens, at the works he started at Landore in South Wales in 1870. The introduction of open-hearth steel, as the foundation for charcoal tin-plates, dates commercially from 1875, when the Landore Works were under the direct management of Siemens. The product of the open hearth process, was classed by the trade as 'soft steel'. Prior to the development of the open hearth furnace, the quality of the steel was not suitable for tin-plate purposes, being brittle and 'springy' instead of being soft and tough; consequently a strong prejudice at first existed against steel.

9.2.4.1. Siemens versus Bessemer debate for base superiority

Strong contention existed for many years on the suitability of steel produced by the Bessemer process, and that produced by the Open Hearth process for tin-plate manufacture. Evidence of this can be found in the report about a paper read before the Iron and Steel Institute in 1886 on the Manufacture of Tin-Plate by P.W. Flower, a manufacturer from Neath in South Wales.(282)

Sir Henry Bessemer F.R.S. was present at the meeting, and he took very unkindly to the remarks by Flower that steel produced by the Siemens open-hearth process was predominantly better than Bessemer steel used for this purpose.

9.2.4.2. Flower's introduction date challenged

Flower in his paper(282) also made several comments concerned with

the historical aspects of the two processes, and the introduction of soft steel as a substitute for charcoal iron in Britain. Bessemer challenged him also on these points at this meeting at the Iron and Steel Inst. in 1886, stating that he had made the first steel tin-plates in 1856, which was nearly twenty years before the stated date of 1875, that had been made by Flower for this introduction. However, Bessemer was not able to supply any proof for this, and the people present did not appear to take Bessemer's word on this matter.

A Mr. James Riley also disputed the 1875 date and Siemens' originality, stating that the only connection that Siemens' had with the Landore Works where charcoal tin-plate had been first developed, was that he was a director of the company, but not in direct control of the manufacturing process. (162) Head challenged Riley on this point stating that Siemens in fact was the consulting engineer.

Apparently Riley at this time had been works manager and was endeavouring to discredit Siemens' work, since as the debate continued, the participants began to get personal and had to be stopped by the President. Analysing the debate, it appears that the process was started by a chemist, who worked in very close connection with Siemens. He had been introduced into the company by Siemens, and could have been influenced by Siemens who was the consulting engineer.

This was one of the very rare occasions during the nineteenth century that the main 'principals' gathered together to discuss the origin of the application of tin to steel. It may be said that of the two processes, the Siemens' process was far more suitable than Bessemer's for the production of the high class steel that was pre-eminently more suitable in tin-plate

Fig. 63 THE WATER PUMP USED BY THE MELINGRIFFITH TIN-PLATE WORKS (1973)

Fig. 64 FURTHER DETAILS OF MELINGRIFFITH WATER PUMP (1973)

Fig. 65 SITE OF THE FORMER TIN-PLATE WORKS
AT MELINGRIFFITH, NEAR CARDIFF (1973)

manufacture. Bessemer steel was cheaper to produce, and had been tried for a short time as a substitute, but was found to be unsuitable. A great advantage of the Siemens' process, apart from the production of 'soft steel', was that it was reliable. Ingots that were produced were homogeneous, but those produced by the Bessemer process were unreliable with a varying metallurgical composition throughout. Although Bessemer may have tried a few experiments in tin-plating steel earlier, it would appear to have been in 1875 that the practical process was initiated.

9.2.5. Some famous Welsh tin-plate works

Records (279) show that in 1858 there was a total of 109 mills in existence, of which a large proportion were located in South Wales.

9.2.5.1. Melingriffith

Among the better - known industrial monuments of the tin-plate industry is the Melingriffith water pump. (Fig. 63 and 64). The Melingriffith Tin-plate Works, (fig. 65), at Whitchurch, three miles north west of Cardiff, were developed on a site first occupied by a forge in 1750 followed by the erection of a tin-plate works adjoining this in 1760.(283)

In Feb. 1768, a Bristol company of ironmasters, Reynolds, Getley and Co., leased Melingriffith and Pentyrch Works and by 1774 Mr. John Partridge had joined the other six partners - nearly all of whom were Quakers. The works was driven by water-power and comprised a forge and two tin-plate mills.

By 1808 the tin works at Melingriffith were described as

THOS. W. BOOKER AND CO., LIMITED.

PRICE CURRENT.

MELIN GRIFFITH WORKS,
NEAR CARDIFF, ... 187

THIS LIST SUBJECT TO ALTERATION WITHOUT NOTICE.

SHEET IRON.

PER TON.

Pen quality Singles to No. 20 not wider than 37 in. £
R. G. „ „ „ „ „ £
R. G. Best „ „ „ „ £
R. G. Best Best „ „ „ „ £
R. G. Charcoal „ „ „ „ £
R. G. Best Charcoal „ „ „ „ £

Doubles No. 24 to No. 24 W. G. 30/- a ton extra. Trebles No. 25 and No. 26 W. G. 60/- a ton extra. Lattens to 30 inches wide No. 27 and No. 28 W. G. 90/ a ton extra. Extra Lattens No. 29 and 30 W. G. to 24 inches wide 20/- a ton each gauge above No. 28 W. G.

Special Quotations given for sizes larger than the above, and for shearing to pattern.

TIN PLATES.

	In. In.	Per Box.	Weight per Box. Cwt.	Q.	lbs.	R. G. Best Charcoal. Perfect.	Produced Wasters.
1 C	14 x 10	225 Sheets	1	0	0		2/- less
1 X	„ x „	„ „	1	1	0		3/-
1 XX	„ x „	„ „	1	1	21		„
1 XXX	„ x „	„ „	1	2	14		6/-
1 XXXX	„ x „	„ „	1	3	7		„
1 XXXXX	„ x „	„ „	2	0	0		„
1 XXXXXX	„ x „	„ „	2	0	21		„
Or	14 x 20	112 „					
S D C	15 x 11	200 Sheets	1	1	27		6/- less
S D X	„ x „	„ „	1	2	20		„
S D XX	„ x „	„ „	1	3	13		„
S D XXX	„ x „	„ „	2	0	6		„
S D XXXX	„ x „	„ „	2	0	27		„
S D XXXXX	„ x „	„ „	2	1	20		„
D C	16¾ x 12½	100 Sheets	0	3	14		2/- less
D X	„ x „	„ „	1	0	14		3/-
D XX	„ x „	„ „	1	1	7		6/-
D XXX	„ x „	„ „	1	2	0		„
D XXXX	„ x „	„ „	1	2	21		„
D XXXXX	„ x „	„ „	1	3	14		„
D XXXXXX	„ x „	„ „	2	0	7		„

R. G. Best Coke a box less than R. G. Best Charcoal. Pen Coke a box less than R. G. Best Charcoal. Wasters at usual difference. R. G. Best Charcoal Terne Plates 14 x 20 2/ a box less than perfect Tin of same size. 28 x 20 in boxes of 112 Sheets double the price of 14 x 20, with an extra of 2/- a box. Pen Terne Plates . a box less than R. G. Best Charcoal Terne Plates.

BLACK TAGGERS.

Pen quality 14 x 10 No. 30 W. G. £
„ „ 31 „ £
„ „ 32 „ £
„ „ 33 „ £
„ „ 34 „ £
„ „ 35 „ £

Pen quality 14 x 10 No. 36 W. G. £
„ „ 37 „ £
„ „ 38 „ £
„ „ 39 „ £
„ „ 40 „ £

R. G. quality 30/- a ton extra.

CANADA PLATES.

Pen quality 24 x 18, 50 Sheets per box No. 26 W. G. £

R. G. quality 24 x 18, 50 Sheets per box No. 26 W. G. £

Including cold rolling and annealing.

TERMS.

CASH—Less 2 per Cent.
Delivered into Trucks at Works or f. o. b. Cardiff.
At Station, Liverpool, 13/4 a ton extra.
Birmingham 11/8 a ton extra.
Manchester 21/8 a ton extra.
London 18/4 a ton extra.
Station to Station in lots of 2 tons and upwards.
Lots of 4 tons delivered alongside in London, and lots of 10 tons in Liverpool without further charge.

TIN PLATES, BLACK TAGGERS, AND CANADA PLATES.

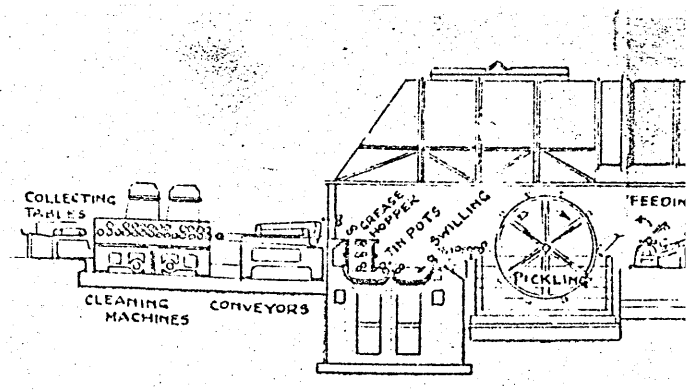
CASH, Less 3 per Cent.—Delivered into Trucks at Works or f. o. b. Cardiff.
In Liverpool 11/4 a ton extra.
In Manchester 21/8 a ton extra.
In Birmingham 11/8 a ton extra.
In London 18/4 a ton extra.
Station to Station in lots of 2 tons and upwards.
Lots of 4 tons delivered alongside in London, and lots of 10 tons in Liverpool without further charge.

Fig. 66 MELINGRIFFITH PRICE LIST DURING THE 1870's (283)

The Melingriffith Co. Ltd.

§

Department.	*Item of Interest*
MILLS . . .	The Cutting of Mild Steel Bars into the required length. Shearing to sizes Opening sheets from pack Eight Steam Mills. Five Water-Driven Mills as follows: 1 Bell Turbine. 1 Water Wheel 3 Driven by a 400 h.p. Horizontal Water Turbine, 16 feet fall Fly Wheel Diameter 36 feet. Weight 120 tons. These three mills have an alternative electric drive.
PICKLING . . .	Grey Type Pickling Machine, with Sulphuric Acid This machine deals with the total 24 hour output of the mills working daytime only. Assorting Packing and Covering
BLACK ANNEALING	First Annealing about 1,000° C. Continuous Tunnel Furnace
COLD ROLLS . .	Eighteen Pairs of Rolls, travelling at about 55 r.p.m., driven by Two Vertical Steam Engines.
WHITE ANNEALING	Second Annealing about 700° C. Continuous Tunnel Furnace



SECTIONAL ELEVATION
THE
THOMAS & DAVIES
(PATENT)
AUTOMATIC TINNING MACHINE

§

FINISHING . .	Four Thomas & Davies (Pa Automatic Pickling, Tinning Cleaning Machines.

§

ASSORTING AND WEIGHING.

§

PACKING—DIFFERENT TYPES.

§

SHIPPING—OVERHEAD GANTRIES.

§

WELFARE . .	Sports Club. :: 650 Voluntar Members.

Sections:

Rugby	Association
Cricket	Boxing
Harriers	Tennis
Provisioning	Skittles
Entertainment	Badminton

§

BRASS BAND . .	Holders of South Wales & Mo Championships.

Fig. 67 THE MANUFACTURING AND SOCIAL ACTIVITIES (283)

AT MELINGRIFFITH TIN-PLATE COMPANY

"perhaps the largest in the Kingdom".(283)

In 1820 Thomas Morgan, one of the workmen, invented a 'crocodile' machine for shearing sheet iron. In 1827 Morgan developed the use of sulphuric acid for black pickling to eliminate scaling, "the plates afterwards to be annealed in an iron box or case".(283) Up until then plates were annealed in an open furnace, both before and after rolling. This proved to be a major step in the development of the industry.

By 1862, steam had been introduced to the mill to supplement water power. The Neath Abbey Ironworks supplied a 26 inch bore engine for the purpose. The manufacture of wire was commenced but was abandoned a few years later.

Fig. 66 illustrates a 'current price' list for tin-plates at Melingriffith during the 1870's.

Fig. 67 shows a very interesting description of both the manufacturing and social activities there.

The 'Melingriffith pot' for coating and tinning was devised in 1893.(284)

From the Western Mail, November 10th, 1887, it was stated:-(285)

"The Tin-plate Trade:- The following notice has been posted at the Melingriffith Works, near Cardiff:-

Owing to the high price of block tin and the low value obtainable for tin-plates these works will be closed on completion of existing orders. Work will be resumed whenever prices will allow for the manufacture being carried on without loss". Regarding the production in 1890,

"The Melingriffith Tin-plate Works consists(286) of seven shears and four water mills, capable of turning out 6500 boxes per week, with sufficient pickling, annealing, cold rolling and

coating power to convert this quantity into finished tin-plates. They are now the oldest works in the trade".

9.2.5.2. Caerleon and Tynewydd

There is no record of when the Caerleon Works near Newport first produced tin-plate, but records show that it was in existence in 1781.(287)

In 1810 the works belonged to a Mr. J. Butler and were producing annually 14,000 to 20,000 boxes of tin-plates, the boxes containing 200 to 300 plates. Mr. Butler was also proprietor of the tin mills at Rogerstone. The plant had 4 mills.

Between 1810 and 1868 there were 5 owners, and during this period there was no record of any substantial extension. In July 1876 the works closed down, and remained so until they were reopened by a Messrs Richards and Hopkins in 1901. Fig. 68 shows a copy of accounts for 1834, and fig. 69 the Memorandum of Association for the Tynewydd Iron and Tin-plate company.(288)

9.2.5.3. Treforest

An interesting pictorial record of tin-plate making from iron sheets is displayed in the Department of Arts at the National Museum of Wales:- The T.H. Thomas collection of water colours. From this pictorial record, it can be seen that it was first necessary to refine the iron which came from the blast furnace, then turn it into wrought iron in a puddling furnace to make it malleable, remove impurities by means of repeated blows of the hammer during shingling, and achieve partial flatness through the tilt hammer before the rolling processes could begin.

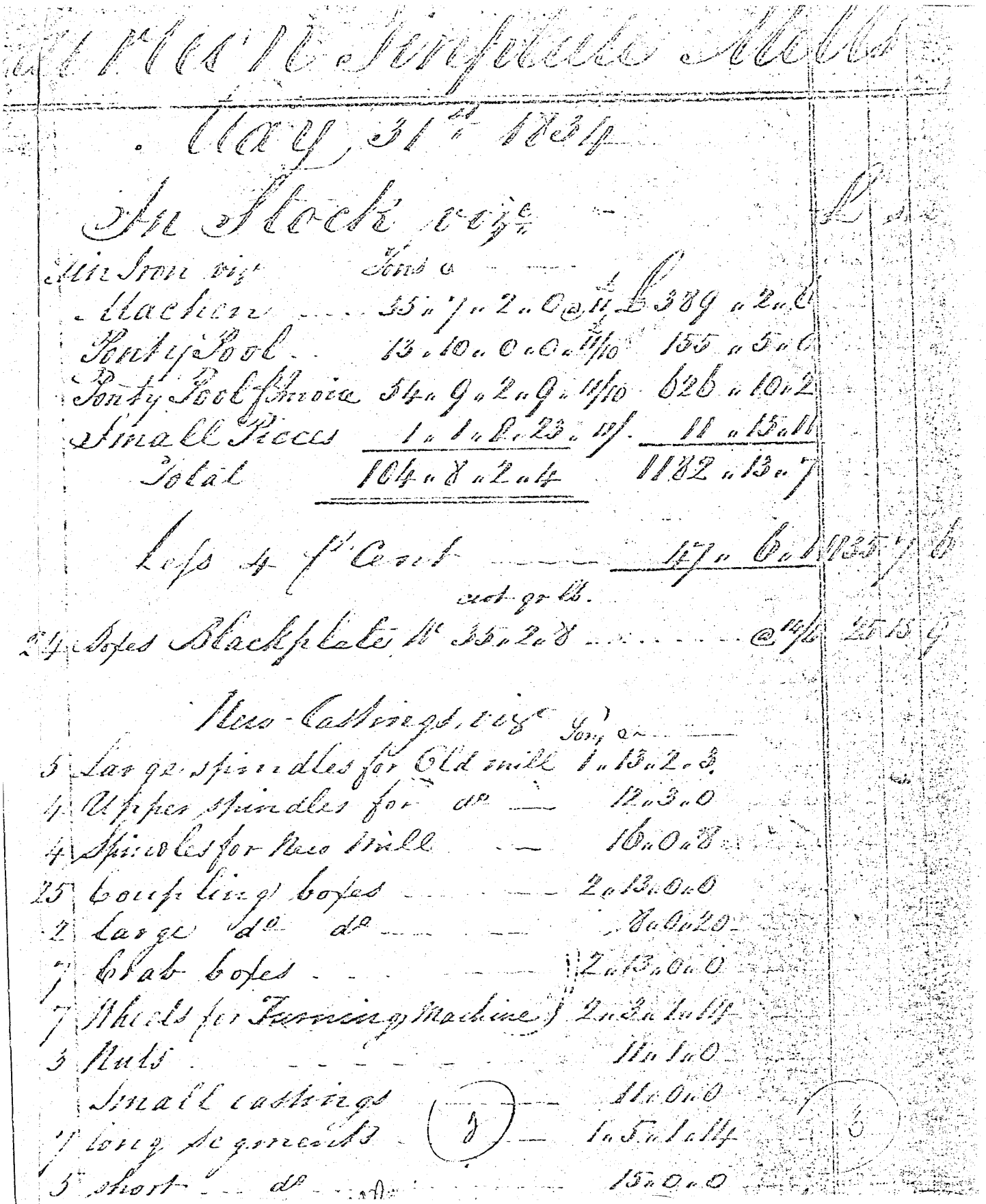


Fig. 68 ACCOUNTS FOR THE CAERLEON TIN-PLATE WORKS FOR 1834 (287)

"THE COMPANIES ACTS, 1862 & 1867."

COMPANY LIMITED BY SHARES.

Memorandum of Association

OF THE

TYNEWYDD IRON AND TIN PLATE COMPANY LIMITED.

1st. The name of the Company is the "TYNEWYDD IRON AND TIN PLATE COMPANY LIMITED."

2nd. The Registered Office of the Company is to be situate in England.

3rd. The objects for which the Company is established are—The taking upon lease land at or near Pontnewydd Railway Station, in the County of Monmouth, or such other land as may be determined upon by the Company from time to time, and the building and erection thereon of a manufactory or manufactories for making iron and tin plates, and any description of goods manufactured of iron or tin, with the necessary engines, boilers, machinery, and plant, and the offices and other out-buildings which may be required in connection therewith, and the erection of a manager's house and workmens' cottages, and the carrying on and conducting the business of iron and tin plate manufacturers therein in all its branches, and with all usual or convenient accessaries, and the doing all such other things as are incidental or conducive to the attainment of the above objects.

4th. The liability of the Members is limited.

5th. The amount of Capital of the Company is Ten Thousand Pounds, divided into Two Hundred Shares of Fifty Pounds each, and with power on increase of Capital to issue Preference and Guaranteed Shares, or Preference or Guaranteed Shares as whole or part of such increased Capital as may be decided upon by Special Resolution.

Fig. 69 MEMORANDUM OF ASSOCIATION FOR

THE TYNEWYDD IRON AND TIN-PLATE COMPANY (288)

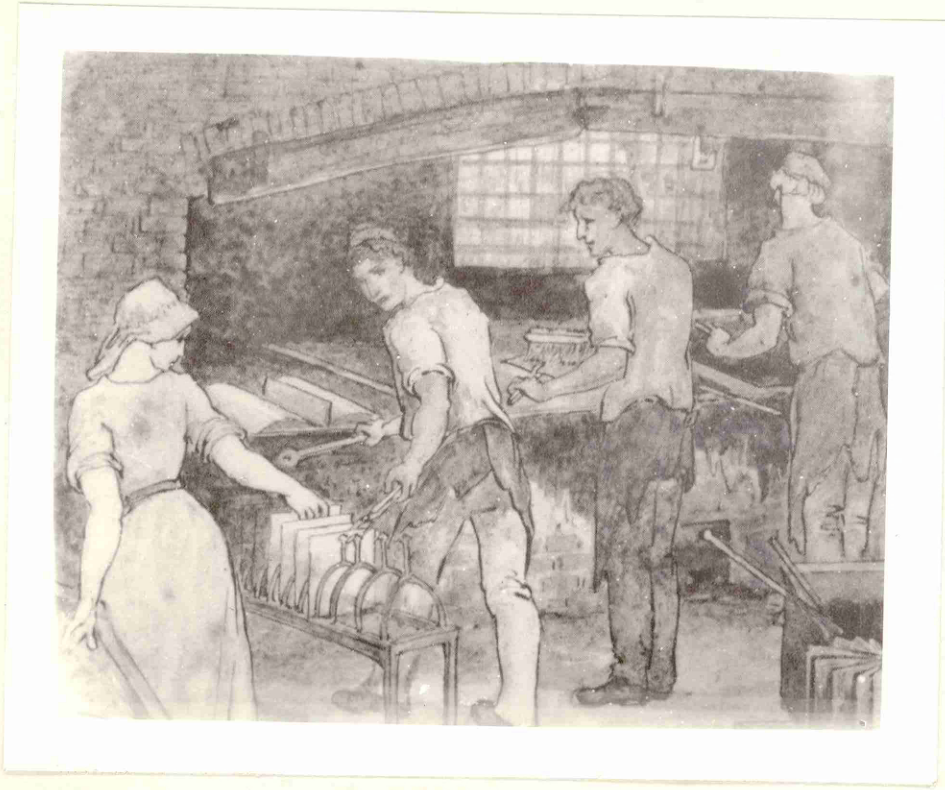


Fig. 70 T.H. THOMAS'S "WASHING AND TINNING THE PLATES" AT TREFOREST TIN-PLATE WORKS

Ack. Nat. Mus. of Wales

Fig. 71 PART OF THE STRUCTURE STILL EVIDENT OF ONE OF THE TINNING BAYS AT THE FORMER TREFOREST TIN-PLATE WORKS (1973)

Fig. 72 REMAINS OF TREFOREST TIN-PLATE WORKS. THE BRICKED UP ARCHWAYS ARE A RECENT ADDITION (1973)

Fig. 70 shows a copy of "Washing and tinning the plates," and Fig. 71 the site of the tinning.

The paintings are of the processes as they were carried out at the Treforest Tin-plate Works, which stood on the Western bank of the river Taff, about two miles south of Pontypridd.

Many of the buildings of the original tin-plate works have survived, and apart from various modifications, such as bricking-up of archways (fig. 72), and light openings in walls, they remain as they were. It is possible still, to reconcile a number of existing internal features with Thomas's water colours such as the tinning bays (fig. 71), which housed the tin pots in the floor, and which were directly ventilated to the outside air by the wide openings in the ceilings, which culminated in chimney stacks.

The tin-plate works originally had waterwheels as its prime movers. These were driven by the waters of a feeder, or water course, channelled to the works from the river Taff at a point about five hundred yards upstream, running for a part of its length through a tunnel in the rising ground which bordered on to the works on the northern side (fig 73). On the works side this feeder was contained by a stone wall which ran parallel and quite near to the building, (fig 72), which housed the rolling machines. At certain intervals in the wall, there are a number of gaps which still contain parts of the structure of the original sluice gate.

William Crayshaw had many problems during the period of his ownership. Chiselled into the wall adjacent to the feeder channel is the word of encouragement to his men 'perseverance'. (Fig. 74)

Fig. 73 ENTRANCE TO THE TUNNEL BRINGING WATER FROM THE RIVER TAFF TO THE TREFOREST TIN-PLATE WORKS

Fig. 74 WILLIAM CRAYSHAW'S WORD OF ENCOURAGEMENT TO HIS MEN

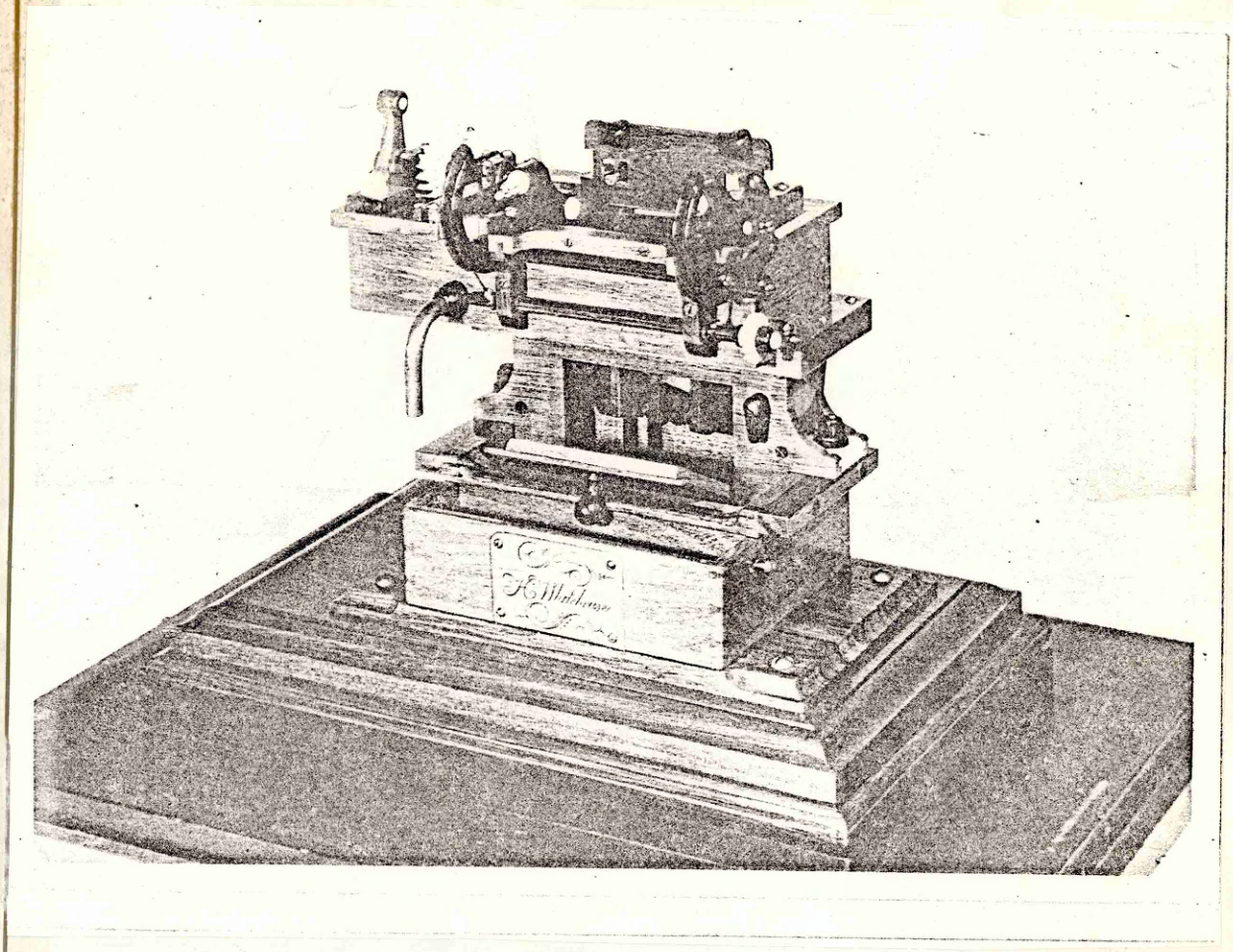


Fig. 75 MODEL OF THE COOKLEY POT

9.2.6. Industry in the Midlands

In the Wolverhampton area the industry was also thriving but on a smaller scale.

According to the 1861 census, there were about 3500 people in the industry in the Midlands. About 1600 of these were at Wolverhampton, somewhat fewer at Birmingham, about 400 at Bilston and a few at Dudley.

Timmins in his section on statistics of Trades published in 1866 stated:- (62) "The tin-plate and japan works in Wolverhampton are large, employing from 250 to 300 hands, of whom fifty to sixty would be young persons, male and female. In the three largest factories of this class, no children are regularly employed.....".

Fig. 75 illustrates the 'Cookley Pot' which was invented by Saunder and Piper at Brierley Hill, Staffs; in which to equalise the coating and remove superfluous metal, the plates were passed between rollers in a grease pot. (62)

9.2.7. System of plate grading

As tin-plates were not manufactured ahead of demand but were rolled to order, they were normally sold without sample by designation. In the course of the nineteenth century a fairly elaborate system grew up: tin-plates were graded according to the material of the iron base, according to the weight of the tin coating, according to finish, according to size and gauge, and according to quality. Thus tin-plates were described as charcoal or coke: deep drawing, deep stamping or ordinary stamping, and as primes, seconds, or wasters. (289) As a further safeguard maker's brand names were developed in the eighteen-seventies

in addition to the merchant marks which had been used for some considerable time. Finally, there was yet another check, independent tin-plate inspectors being employed to examine consignments to see that they were up to specification. The inspector was responsible for checking the quality of the plates, the number of plates, and also the packing and marking of the consignment. Terne plates were plates coated with a mixture of lead and tin, about two thirds of the former to one third of the latter. Black-plates were the sheets of iron before they were tinned. Tin-plates were divided into two qualities i.e. coke and charcoal, the former produced from bar iron made by puddling pig iron in the ordinary puddling furnace, the latter from bar iron made by melting pig in the charcoal furnaces.(289)

9.2.8. Complementary shipping arrangements

Until about 1870 tin-plates were shipped coastwise from Llanelly, Swansea, Neath, Port Talbot, Cardiff, and Newport for export to Liverpool or, in smaller quantities, to Bristol. Both towns had regular shipping connections with the overseas markets. Liverpool had a further advantage as the outlet for Lancashire. Since tin-plates were packed in timber boxes which were heavy and compact, cotton piece goods, which were bulky and relatively light, formed an excellent complementary cargoe. For many years Liverpool was the chief port for the trade in the U.S.A. In 1875 90,618 tons of plate were shipped to America.(289) Exports in the years between 1870 to 1875 are given in fig 76.

9.2.9. Finance for expansion

Since the period of manufacture was comparatively short - about fourteen days - a manufacturer could operate with

	CWTS.	VALUE £
1870	1,997,019	2,362,872
1871	2,392,116	2,900,625
1872	2,364,684	3,812,744
1873	2,412,760	3,953,042
1874	2,459,200	3,714,810
1875	2,771,260	3,691,382

FIG. 76 EXPORTS OF TIN-PLATE TO AMERICA BETWEEN 1870 - 1875 (289)

little working capital. But as such, makers were forced to rely on immediate sales. Manufacture on this basis enabled the merchants virtually to dictate prices. Although the merchants appeared to be few in number, the tin-plate works by the second half of the nineteenth century had become many.

Bars were paid for on the 14th (and later the 30th) of the month following delivery, while the makers received payment for sales of tin-plate in fourteen days (less 4 per cent = 3 per cent discount and 1 per cent commission).(289) Nearly all the works were financed by bank loans and because it was relatively easy to build a small tin-plate works and to obtain credit and advances to run it, an over-optimistic view was sometimes taken of the prospects of the industry. The chief role of the banks was in the provision of working capital. During the period of its existence, the Swansea branch of the Bank of England, for example, granted accommodation to tin-plate workers and the Glamorgan Banking Co., assisted Hallam and Madge of Morriston.(290)

9.2.10. Challenge from Germany

An insight into the operation of the industry was given by Ernest Trubshaw of Llanelly in a paper to the Iron and Steel Institute:-(71)

".... The manufacture of tin-plates may be considered a speciality of this country, as the quantity now made abroad is comparatively unimportant. Plates are made to some extent in France and Germany, and attempts have been made to establish the manufacture in America, but with very limited success".

However Bowen in his book Rise, Progress and Future of the Tin-plate Trade published in 1892 stated :-(268)

"The tin-plate people in 1887 became alarmed at the increased production of tin-plate in Germany. In that year, it was said that spies had succeeded in getting into the Welsh works, and had learnt the secret of tin-plate making with its latest patents etc; but there was no truth in such reports, although Germany is at the present time doing all in her power to recover the trade she lost in 1670".

Bowen goes on to say:- (268)

".... The year 1882 will long be remembered in the trade as a year of misery. Two works stopped payment, with liabilities of £173,000, followed by another two with £142,000 and another with £56,000. Great distress prevailed. A central Relief Fund was formed, which was the means of preventing much suffering".

Suffering had been no new experience for the tin-plate workers. A strike which had been nationwide in 1874 had caused great hardship amongst the workers' families.

9.2.11. Formation of Tin-plate Workmen's Association

In the year 1880 Bowen relates that a Tin-plate Workmen's Association was formed. This helped to solve many disputes between workmen and employers. A Mr. William Lewis was the secretary.

".... He had upon one occasion a narrow escape from being mobbed by the workmen's wives, who blamed him for being the cause of the men being locked out, but Lewis escaped the women, by not appearing at the place where he was announced to speak; if he had done so he would have had a warm reception". (268)

9.2.12. Production in the 1880's

An insight into the development of the industry by 1880 was given by Trubshaw.(71) During the course of the century it was evident that the process had become far more mechanised particularly relating to the sheet manufacture prior to the preparation and tinning process.

The bars were now heated to a dull red, passed through the mills, doubled, re-heated and rolled once again until the required lengths and gauges were obtained. This processed earlier on in the century had been performed by hand but with mechanisation, the work force required could have been considerably reduced.

At the pickling stages Trubshaw mentions that some manufacturers were now using hydrochloric acid. This form of pickling was a progression from earlier on in the century.(68) The process of pickling was now also carried out by machinery whereas previously it had been carried out by hand. Trubshaw describes one of these machines:-

"... There are from ten to twelve boxes of plates pickled at one time. They are deposited in cradles or racks and moved up and down to and fro in a bath of acid diluted with water. In one simple and compact machine the movement of the cradles is effected by means of a single acting cylinder fixed in the centre of a cast iron pillar. The steam valve used in working the cradle is worked automatically by means of a lever and weight, the arms of which are struck by a tappet, so that in rising the steam is cut off, and in descending is let on, so confining the stroke to the required length. In about 5 minutes the plates are sufficiently clear, and the cradle is then raised out of the acid and passed round to a tank containing water. Pickling and swilling is carried on at the same time, and spare cradles

are provided for filling and emptying, so that no delay occurs.

".... The plates having been thoroughly swilled to remove all traces of acid, are sorted with a view to preventing any sheets going forward that are not properly pickled. They are then packed in wrought iron boxes termed pots and are placed in a furnace for the purpose of annealing where they remain under the action of a slow fire from eight to ten hours.(71)

".... Having been removed from the furnace and allowed to cool, the plates are passed on to the cold rolls. The object of this process is to produce a finely polished surface, and when this is efficiently done, a considerable saving in tin is effected, and the plate looks all the better in the finished state. The pressure in the cold rolls having hardened the plates, they are again packed in pots, and undergo a second annealing. Cast iron pots are used, the heat not being as great as on the first occasion. The sheets are allowed to cool, and in this state are called 'finished black plate'.

".... The coating process is a most important one, and is the next step necessary for the converting of the finished black plates into tin-plates. A set of five cast iron pots is provided, erected over flues, side by side. The first one is called the grease pan and contains melted palm oil or tallow; the second contains molten metal, and is known as the tinman's pot; the third and fourth contains molten metal and are known as the washman's soaking and dipping pots; and the fifth contains grease".

From this description by Trubshaw it can be seen that the

sequence of operations had not altered from Parkes' description in his letter of 1819.(68)

However, important improvements had taken place. Formerly the plates had been placed in a rack for the superfluous metal to drain off, but two important improvements had been patented which avoided this. In the former process the thickness of the coating was determined to some extent by the time the plates remained in the hot grease. The process was very wasteful, and it was impossible to obtain a uniform coating over the surface of the plates.

In his patent of 1883 on 'Coating Metal Plates with Tin etc'. Edward Morewood of Llanelli stated:-(291)

"The object of this invention is to so operate by mechanical means and appliances upon the sheets of metal emerging from the bath in which they are coated as to dispense with the 'wash pot or brush over', and to yield covered sheets free from 'scurff' and imperfections, and with a better finish than is otherwise given. This is accomplished by causing the sheets as they emerge from the bath to be guided by rollers, covered with molten grease so as to avoid exposure to the air between 'washing rollers' kept covered with molten metal.(291) The washing rollers did not bear on the sheet, but were so closely adjusted as to wash off the scum and refuse on its surface. On leaving the washing rollers the plate, still passing through a bath of grease to prevent exposure, is passed through 'finishing rollers' to remove the excess of metal, and finally through a pair of 'improving rollers' which bear against each other by means of springs and thus lightly nipping the sheet between them impart a smooth surface and finish to the metallic covered sheet".

This development proved to be a major breakthrough in the mechanisation of the industry. It had far reaching effects including its use, in an adapted form, in the galvanizing industry.(292)

A machine of the vertical type was invented by Taylor and Leyshon in 1882.(293)(294) (Fig. 77)

It was the first single pot developed for coating and finishing without the aid of the washman, to meet with practical success and Hammond as late as 1897 stated that machines of this type were still widely used.

The principle employed was that of drawing or pulling the plates by means of a nipping appliance working beneath the surface of the metal, through the flux into the tin in a vertical direction, so as to allow the plate to clear itself of any scruff adhering to it.

The plates entered and left the pot perfectly flat, and a coating of any quality could be produced, by regulating the speed of the rolls in the grease-box and by the quality of tin in the troughs under the finishing rolls, which tended also to wash off any scruff taken up in the tin pot. The machine was simple in construction and was made to various dimensions to suit the sizes of plates to be dealt with. It was specially adapted also for thin plates. One of the thinnest sheets of tin-plate to have been rolled, according to Bowen,(268) was one .0038 inches at Llanelly.

When black plates had to be coated, an additional process known as white pickling had to be followed:-(71)

".... To prepare the surface for the adhesions of the metal, and to remove the water left on the plate from the swilling, they are immersed in the palm oil in the first pot for some three or four minutes, about 28 times a sheet at a time.

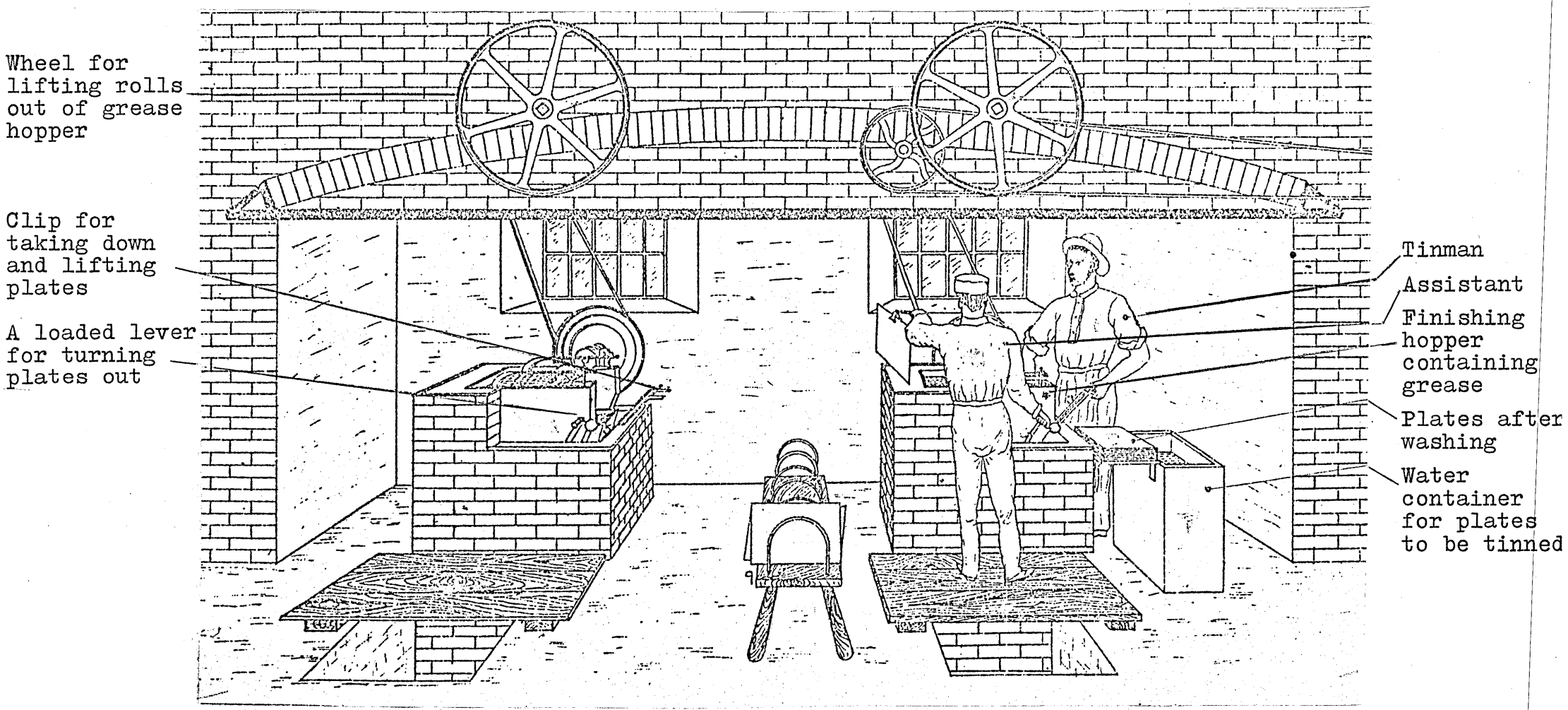


Fig. 77 TWO COMPLETE TAYLOR AND LEYSHON TINNING MACHINES (293)

They are then transferred from the palm oil to the second pot, where they remain about another four minutes. They are afterwards handed to the washman, who brushes them to remove scruff from the surface.

It is of note that in the vertical machine the washman had been dispensed with, consequently this would only have applied to the 'conventional' machines.

".... The plates were then immediately dipped in a second bath of metal at a lower temperature and passed through the rolls in the fifth pot. A boy receives them from the rolls, and they are then ready for cleaning, which is effected by pushing them to and fro in bran, and by rubbing them in sheepskin".

It is of note that use was being made at Llanelli at that time of sheepskin. This material would have been in ready supply in that area, since sheep farming was predominant there at that time.

At this stage in his deliberations Trubshaw (11) made a prophecy which most certainly came true. Speaking of tin-plating with the aid of electricity he stated "Possibly this method is only in its infancy, and ere long more may be heard of it". This appears to be the first recorded statement about electrolytic tin-plate.

9.2.13. Royal Commission of 1885

In 1885 a Royal Commission was set up to investigate the (Depression in many Trades and Industries.)

A circular was sent to all the principal commercial associations ranging from Agricultural Engineers Association to the Linen Merchants Association and including the Tinplate Manufacturers Association.

Fig. 78 shows a copy of the standard letter and also

APPENDIX B.

CIRCULAR ADDRESSED TO THE PRINCIPAL COMMERCIAL ASSOCIATIONS.

Royal Commission on the Depression of Trade and Industry,
8, Richmond Terrace, Whitehall, S.W.,
7th September 1885.

SIR,

I AM desired by the Royal Commission on the Depression of Trade and Industry to forward to you the accompanying paper of questions, which has been drawn up with the view of obtaining information as to the present condition of Trade in this country, and of eliciting the facts of the situation into which the Commissioners are directed to inquire.

Any answers which your Association may desire to return should be written opposite the questions to which they relate, and should be confined within the limits of the enclosed paper.

The Commissioners would be glad to receive your replies, if possible, by the end of this month; and it is particularly requested that the answers to the earlier questions may not be delayed in order to reply to Nos. 11 and 13, as it is of importance to have the information with regard to matters of fact as early as possible.

I am to add that the two latter questions are intended rather to suggest special points on which your Association may desire to offer observations than to elicit exhaustive replies on all the topics mentioned; and I am to ask that the answers, both to these and to the earlier questions, may be drawn up in as concise a form as possible.

Further copies of the questions can be obtained if required.

I have the honour to be,
Sir,
Your obedient Servant,
(Signed) GEO. H. MURRAY,
Secretary.

The Secretary of the
Association.

QUESTIONS.

1. In what branches of trade or industry is your Association specially interested?
2. In what proportion do they find their market at home, and in foreign countries; and, as regards the latter, in which countries chiefly?
3. How have they been affected in the last five years as compared with the periods 1865-70, 1870-75, 1875-80, in respect to—
   (*a.*) Volume;
   (*b.*) Gross value;
   (*c.*) Net profit;
   (*d.*) Amount of capital invested;
   (*e.*) Quantity of labour employed?
4. The phrase "depression of trade" would appear to imply a "normal level" of trade. During what periods in the last 20 years should you say that trade had been—
   (*a.*) At its normal level;
   (*b.*) Above that level; or
   (*c.*) Below it?
5. Judged by a scale constructed in this manner, can the condition of the branches of trade or industry in which you are specially interested be fairly described at the present time as "depressed"?
6. If so, when did the depression begin; when did it reach its lowest; and what are its most prominent symptoms?
7. Has its progress hitherto been uniform or irregular; and what do you anticipate that its course will be in the immediate future?
8. Are there any special circumstances to which the existing condition of the special trade or industry of your Association can be attributed?
9. Should you say that—
   (*a.*) The demand for,
   (*b.*) The supply of,
   (*c.*) The return on
   capital in your trade or industry is above or below the average of the last 20 years?
10. Is the rate of wages in relation to service rendered, and to the quality and quantity of the work produced (*a*) for skilled and (*b*) for unskilled labour in your trade or industry, above or below the average of the last 20 years?
11. What measures could, in your opinion, be adopted to improve the existing condition of your trade or industry (*a*) by legislation, and (*b*) independently of legislation?
12. To what extent do you consider that the present condition of your trade or industry has been affected by the operation of any of the following causes:—
   (*a.*) Changes in the relation between capital and labour;
   (*b.*) Changes in the hours of labour;
   (*c.*) Changes in the relations between the producer, the distributor, and the consumer;
   (*d.*) Fall in prices, or appreciation of the standard of value;
   (*e.*) The state of the currency and the banking laws;
   (*f.*) Restriction or inflation of credit;
   (*g.*) Over-production;
   (*h.*) Foreign competition;
   (*k.*) Foreign tariffs and bounties;
   (*l.*) Incidence of taxation, local or imperial,
   (*m.*) Communication with other markets;
   (*n.*) Legislation affecting trade;
   (*o.*) Legislation affecting land?

FIG. 78 CIRCULAR AND QUESTIONS ASKED BY THE ROYAL COMMISSION TO THE PRINCIPAL COMMERCIAL ASSOCIATIONS

TINPLATE MANUFACTURERS' ASSOCIATION.

1. In the manufacture of tinplates, of which we produce 8,000,000 of boxes of a hundredweight each, the value of which may be taken as 6,500,000*l.* a year.

2. Three fourths of the whole production are exported. Our great market is the United States, where they are used in making utensils as a substitute for earthenware, in roofing instead of slates, in packing petroleum, and in canning meat, fish, and fruits of all kinds. More than half of our total output is thus consumed in America. All other countries take more or less, but none on a very large scale.

Owing to the extreme cheapness and utility of the article, and the multitude of uses it can be put to, our export trade increases steadily at the rate of about 350,000 boxes a year. This is not the case with the home consumption, which is stationary and lifeless.

3. During the last five years our trade has increased in volume, as stated in reply to No. 2, and with the increase in volume there is an increase in gross value, but not in due proportion. As regards net profit, although special skill or advantages have enabled some manufacturers to make money, the trade as a whole has been unprofitable.

There are 84 works in Wales, which is the seat of this industry, and more than 30 of them, chiefly of the smaller class, have failed during the last five years.

4, 5, 6. In our trade, which constantly grows, as stated, it is difficult to fix upon a "normal level." In 1872 there was a great inflation in the prices of metals. Large profits were made, which led to the erection of new works and extension of old ones. In consequence when the re-action came the market was crushed down by over-production, which weighed upon it for years. In like manner in 1879 there came a "boom" from America, which sent up the price of the lowest quality to 30*s.* per box. Again for a short time large profits were made, which sent up 101 new mills. Ever since the trade has been suffering from the effect of this, with a declining market, which this year fell as low as 12*s.* 9*d.* per box.

This price being below the cost of production, a combination was formed to reduce production by stopping one week in every month to the end of the year. This combination has been in operation for three months, and has greatly improved the market.

7. The course of our trade, as stated, has been one of regular growth in consumption but of great irregularity in respect to profit. As regards the future it will greatly depend on whether Germany will appear as a competitor. There are reasons to expect this, as they have made great advances in producing steel by the Basic process. With it and with lower wages and longer hours of work they would be most formidable competitors.

8. None other than those set forth.

9. As stated the demand for our manufacture has increased, and the supply or power of production has increased in a greater ratio. Hence the return on capital is much below the average of the last 20 years.

10. Our wages are controlled not by supply and demand but by a trades' union. They are almost entirely paid by piecework, so much per box, and the rates are the same as were paid 30 years ago. During that period improvements in plant have doubled the output of a mill, and we have men earning 50*s.* to 60*s.* a week for eight hours work, and youths of 19 or 20 getting 35*s.* to 40*s.* a week. These extravagant wages are kept up by the union, and go on just the same whether the manufacturer be making a profit or losing money by every box he makes.

11. The great cause of depression in our trade is over-production, for which we are ourselves to blame. There are, however, other causes, the result of legislation. Every Act of Parliament passed of late years in connexion with trade, however well intended, has had for its effect an increase in the cost of production.

The Act which sanctioned trades' unions that were formerly illegal — being, as they are, "in restraint of trade"—has enhanced the cost of every manufacture they control. In another direction legislation has brought about the ruin of the agricultural interest, which interest is the corner stone of the home trade. In common with other manufacturers we suffer by the crippled condition of the home trade, for whilst we have a growing and active foreign demand, that of our own country is stationary and stagnant.

(Signed) JAMES SPENCE,
President of the Tinplate
28th September 1885. Manufacturers' Association.

FIG. 79 REPLY TO THE ROYAL COMMISSION FROM THE TIN-PLATE MANUFACTURERS ASSOCIATION

of the questions asked by the Commission.

Fig. 79 gives the reply from the Tin-plate Manufacturers Association.

It illustrates the inherent problem that the industry had. In times of 'boom' it was possible for new manufacturers to set up plant with relative ease which caused overproduction during periods of slackness.

There is also the fear expressed about Germany appearing as a competitor. At this time the German industry was on the upsurge.

In an article (295) in Dingl.J on the Manufacture of Tin-plate in 1884, F. Stott 'sketches' the processes adopted in the German tin-plate industry.

The description indicates that the development of the industry was in an advanced form and very similar in technical detail to that present at that time in Britain.

Manufacturers in Britain however were sufficiently confident in the future of the industry as to contemplate expansion.

A report in 1886 (296) stated that:-

Iron and tin-plate workers of South Staffordshire are desirous of increasing their tin-plate manufacture, but heavy rail rates and the importance of being near to a cheap and plentiful supply of steel, have determined not to extend their present works but to erect new premises near Newport, Monmouthshire.

9.2.14. America's indifferent start

James Spence, President of the Tin-plate Manufactures Association in his reply to the Royal Commission stated that three fourths of the whole production of tin-plate was exported. More than half of the total output was consumed

in America.(72)

Early efforts to establish a tin-plate industry in the United States had only had limited success in contrast to the success of the Welsh industry during most of the nineteenth century. All tin-plate had been imported, and it had never been subjected to duties as was the case on other iron and steel products being manufactured in the United States. A duty of 0.5c. a lb. was imposed by an Act of 1862 and retained until 1864 becoming 2.5c. a lb. at that time, but the increase was never put into effect.

William Banfield recalled:-(72)

"My father operated the first tin-plate mill in America which had been built in 1872 by William Rogers, who had received his training in England. In the spring of that year Charles Banfield, my father emigrated to the United States and settled at Appolo, Pa., where two sheet mills were built. My father rolled the first heat of tin-plate made in the United States and I was his heater".

This statement was probably not strictly correct since earlier attempts had been made but not on a commercial scale.

"In 1873 two tin mills were erected in Demmler, Pa., and one in Wellsville, Ohio. However in that year one of the mills at Demmler had to close down after only one weeks operation. These were the days of iron, before soft steel was introduced, and far more skill was required in the production. Also the wages were far higher in this country, (United States), than they were in Great Britain, the manufacture was abandoned for some years".

The main uses for tin-plate in America at this time were in

the tin roof and canning trade.

Canning had been a small business until the American Civil War. At that time, Lincoln called hundreds of thousands of Northern troops into the field. Men were taken to the South from their Northern homes and on arrival found that little food was available.

This proved to be a great impetus for the canning industry inparticular, and the tin-plate industry in general.

Attempts were made to take the trade to America by giving incentives to Welshmen to go and set up the industry there. Bowen stated:- (268)

"It is well known that there are no skilled tin-plate operatives in this country, says the Americans. Will it not be necessary, therefore, for a proper prosecution of the new enterprise that these operatives be brought from Wales".

As soon as it became evident to Welsh manufacturers that the developing American industry was becoming a formidable competitor, they began to reduce their prices until the prices became so low that American firms, with their higher wages bills were unable to continue manufacture without loss. They were not re-opened for the manufacture of tin-plate until the passage of the Mc.Kinley Law in 1890, a period having elapsed of from eleven to twelve years.

9.3. AMERICA'S INDUSTRIAL CHALLENGE (CIRCA 1891 - 1900)

9.3.1. Mc Kinley's tariff

By the late nineteenth century the Welsh tin-plate industry had become so dependent upon the American market for its exports that the passing of the Mc.Kinley tariff came as such a body blow to the industry that it despaired of any recovery. (297)

William Mc Kinley who later in 1897 became President of the United States had been a major in the United States Volunteers

Year.		Gross Tons.	Year.		Gross Tons.
1871	...	82,969	1887	...	283,836
1872	...	85,659	1888	...	298,238
1873	...	97,177	1889	...	330,311
1874	...	79,778	1890	...	329,435
1875	...	91,054	1891	...	327,882
1876	...	89,946	1892	...	268,472
1877	...	112,479	1893	...	253,155
1878	...	107,864	1894	...	215,068
1879	...	154,250	1895	...	210,545
1880	...	158,049	1896	...	119,171
1881	...	183,005	1897	...	83,851
1882	...	213,987	1898	...	66,775
1883	...	221,233	1899	...	58,915
1884	...	216,181	1900	...	60,386
1885	...	228,596	1901	...	77,395
1886	...	257,822	1902	...	60,115

FIG. 80 IMPORTS OF TIN-PLATE INTO THE UNITED STATES. FROM WALES. NOTE THE DECREASE AFTER 1891 AS THE AMERICAN INDUSTRY BECAME ESTABLISHED.(297)

under Lincoln and had risen to be Chairman of the Ways and Means Committee. For some years the British manufacturers had no competitor from any other country apart from Germany and the trade had increased enormously. The output doubled every ten years, till in the years 1887 - 90 the average yearly exports amounted to 399,329 tons of the value of £5,682,641. Of this quantity the United States took as much as 304,695 tons, of the value of £4,278,667 (297) (fig. 80.)

The American market ensured for British manufacturers the most speedy return and the largest margin of profit.

On October 1st 1890, the Mc Kinley tariff became operative, though the section dealing with tin-plate did not become operative until July 1891. Up to that time, the import duty on tin-plates was only £4.6 per ton. The new tariff immediately raised it to £10.12 per ton.

In spite of the tariff however, the Welsh export of tin-plates to the United States did not immediately cease. The American manufacturers were not able for a year or so to cope with home demand. They required time to build their works, to establish machinery and to train their workmen. (297)

The annual average of British tin-plate exports to the United States in the years 1887 - 80 was 304,695 tons, valued at £4,278,667. The annual average in the years 1892 - 93 after the Mc.Kinley Tariff was 267,040 tons valued at £3,527,568.

In 1889 only about 40,000 tons, or less than a tenth of the whole output was required for the home market, so that when the Mc.Kinley Tariff was passed the outlook appeared so gloomy that several of the leading Welsh manufacturers emigrated to America and constructed new works over there.

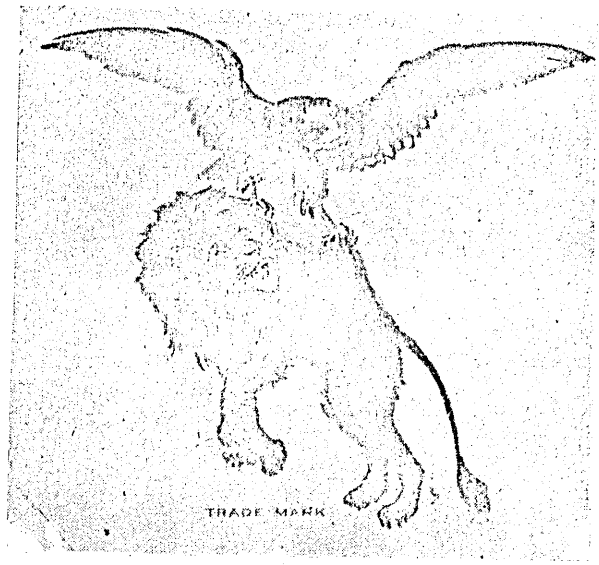


FIG. 81 TRADE MARK OF THE AMERICAN TIN-PLATE CO. ELLWOOD IND. 1891. THE AMERICAN EAGLE CARRYING THE BRITISH LION SYMBOLIZES THE REPLACEMENT OF WELSH TIN-PLATE BY THE AMERICAN PRODUCT AFTER THE INTRODUCTION OF Mc KINLEY'S TARIFF IN 1891 (297)

The Mc.Kinley Act had as one of the stipulations that the duty would be removed completely if the American industry failed to produce a certain amount of plate by June 30th 1897, namely that the amount of tin-plate produced in any one year between July 1st 1891 and June 30th 1897, had to equal one third of the plate imported during any fiscal year of this period. If this provision was not met, protection was to cease.

Mills rolling light gauge sheets hastily installed tinning equipment and other rolling mills were built with the necessary finishing facilities. Approximately 20 plants began operation in 1891.

Fig. 81 illustrates the Trade Mark of the American Tin-Plate Co., Ellwood, Ind. in 1891 The American Eagle carrying the British Lion symbolizes the replacement of Welsh tin-plate by the American product.

9.3.2. Welsh labour helps to develop American industry

During the first few years of manufacture in the United States the industry was forced to rely upon Welsh methods and labour to a considerable extent. One of the greatest obstacles was the breakage of equipment, most of which had been imported from Wales.

In a discussion held in 1897 at the Iron and Steel Inst. Sir John Jenkins M.P. gives an indication as to how the Welsh industry reacted to the loss of the American market:- (298)

".... But although there had been a constant decrease since 1891, chiefly due to the action of America, it was satisfactory to find that their exports to other countries had been increasing at a very rapid rate indeed. Exports to Germany showed an increase of about 133 per cent. Although, however, the percentage of increase to other countries was

large, it was a percentage on a much smaller quantity than was formerly shipped to America. If the increased shipments went on at the same rate as during the last eighteen months, they would regain in eight years from the present time, if not earlier than that, the position they held in 1891."

9.3.3. American and Welsh techniques compared

During the last decade of the nineteenth century a great change took place in the tin-plate. This was with the general adoption of mild steel as a substitute for iron bars, which were formerly produced in the charcoal and puddling forges attached to the tin-plate works. The result was that these forges became entirely abandoned.

As the industry in the United States developed, new techniques were introduced. Whereas in Wales at this time two pairs of rolls had been used, the first for roughing the steel and the second for finishing the plates, in America only one pair of rolls was used in the mill, the operation of roughing down and finishing being performed in the same pair. In some cases three pairs of rolls were employed in two mills; one pair roughing down and two finishing.

Another variation that developed in America was to have a greater diameter and length of hot mill rolls. It was found that there was a greater heating efficiency and that more pressure could be exerted. The black plate for tinning was hot rolled from bars into two sheets which were doubled and redoubled with intermittant heating and rolling. With the larger rolls it was also possible to maintain a more uniform and constant temperature.

Another development that was described by Hammond was the introduction of the Thomas - White "half-circular" machine for tinning, (fig. 82).

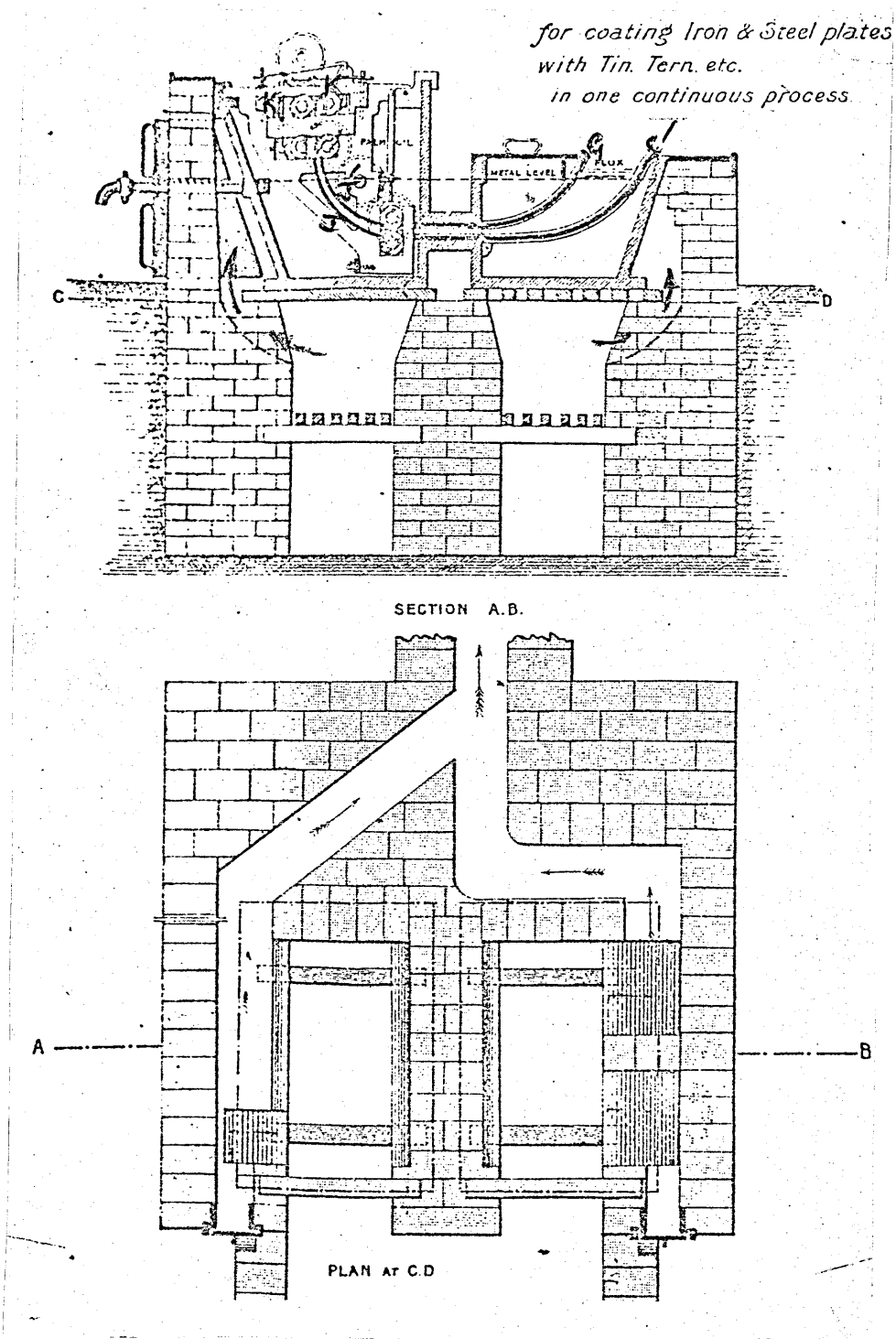


FIG. 82 THOMAS AND WHITES TINNING MACHINE (292)

The molten tin occupied the space in the lower part of the pot with the flux lying on the surface of the tin at the feeding end.

The plate was inserted by the tinman between the iron bars which formed the guide G G', and passed through the flux into the molten metal. It was moved on by a light iron rod held by the tinman until it reached the revolving rolls H, from which it was conveyed forward through the guides J J' out of the tin and into the finishing rolls K K' revolving in the grease. The plate coming from the rolls was then placed by the 'grease-boy' in a rack for removal by the dipper.

Hammond stated:- (292)

"Plates of any length can be coated in this pot; the makers inform me that they have satisfactorily coated experimentally one continuous length of plate 6 inches in width and 150 feet long".

9.3.4. Worshipful Company of Tin-plate Workers

Throughout the nineteenth century the Worshipful Company of Tin-plate Workers of the City of London continued to thrive. Throughout much of the nineteenth century, the Clerkship had been in the hands of Edward Burkitt and his son Edward, who had been between them in charge of day to day affairs between 1838 and 1891. A distinguished antiquary James Curtis was then appointed, and after a brief tenure of office, he was succeeded by Ernest Ebblewhite from 1894.

It is recorded that he brought vigour and colour into the affairs of the Company. He had only been in office a few months when he was instrumental in organising the Company's contribution to the Lord Mayor's show.

The procession for that year included three carriages with

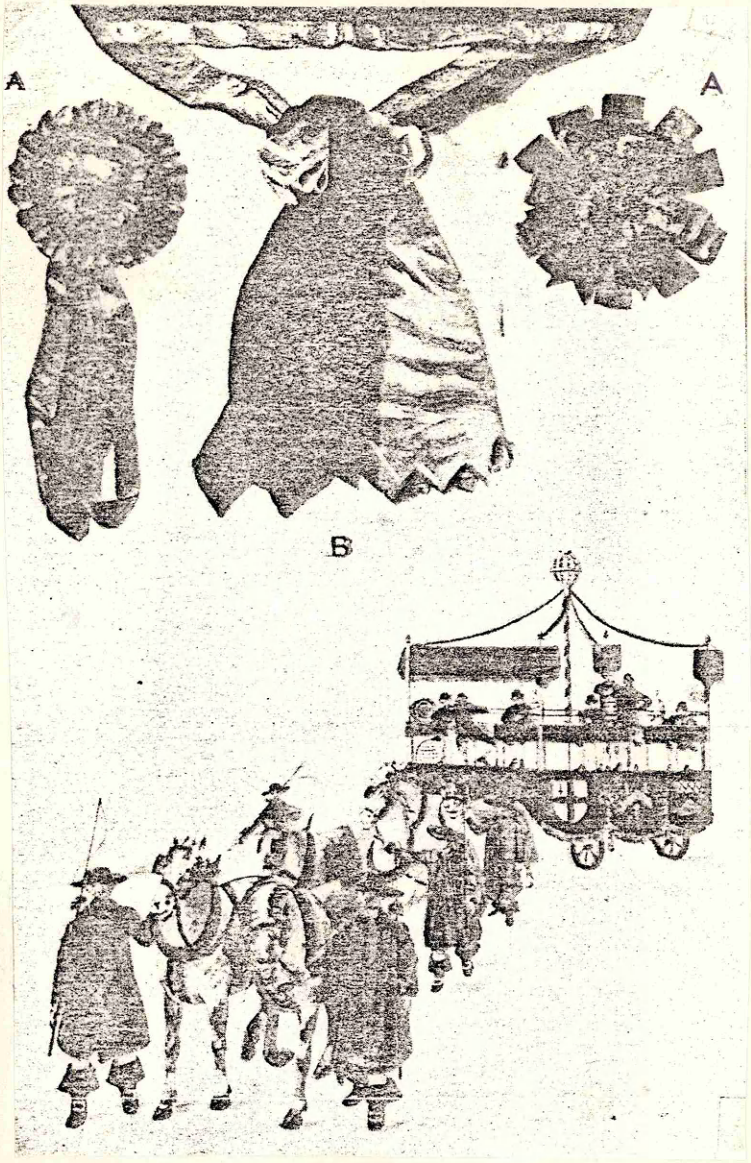


FIG. 83 THE WORSHIPFUL COMPANY'S CAR IN THE LORD MAYOR'S PROCESSION 1894 WITH THE BEADLE'S SASH (B) AND ROSETTES WORN BY THE CARTERS AND HORSES (A A)

(299)

representatives of the Company, the Master, Clerk and several members of the court being drawn by horses decorated with rosettes of the Company's colours, the Beadle accompanying them with his mace, his gown, and a decorative sash. (Fig. 83).

9.3.5. The Welsh find new markets

To step back from the colourful scenes of the Lord Mayor's procession to the bleak reality of the industry in South Wales, the concluding years of the century were devoted to finding fresh outlets for the tin-plate now that American market had effectively closed. Despite the loss of the American domestic market the industry retained its virtual monopoly of the world trade in tin-plate.

By 1894 the American manufacturers had found their feet and were able to supply the home demand without the aid of the Mc.Kinley tariff. On August 1894, the Wilson tariff of £5.52 per ton took the place of Mc Kinley tariff of £10.12 per ton. The reduction in the duty did not diminish the American output. In fact it went up in 1895 - 96 to 137,014 tons, while the British exports fell to 168,063 tons. (297)

Though the American production had grown to such a large extent, on July 24th 1897, there was still another change made in the tin-plate tariff. By the Dingley tariff of that date the import duty was raised from £5.52 per ton to £6.90 per ton and at that value it remained for the rest of the century.

The British industry had been brought very near to ruin by the application of hostile tariffs. Inparticular the Welsh tin-plate trade was deliberately aimed at by the American protectionists. They had a unique opportunity and

took full advantage of it, since the American consumer was willing to pay the price.

The Welsh industry had had use, enterprise and initiative for over a century and this was just another obstacle that had to be overcome. They soon found a way of readjusting their industry to new requirements. They discovered new markets, and developed the home market which in more flourishing days had been somewhat neglected.

Although the American industry had relied heavily on centuries of experience gained by the Welsh industry, they began to develop their own techniques and soon a viable industry emerged.

On the 28th August, 1894, the enactment known as the Wilson Bill became law. The duty on tin and terne plates was reduced from 2.2 to 1.2 cents per pound. The duty on black plate, which, under Mc.Kinley law, had been 1.65 cents per pound, was placed by Wilson at 1.225 cents per pound.(300)

During the financial year ending June 1895, 48 firms were producing, and the amount of tin and terneplate amounted to 194,000,000 pound. One year later, 74 firms were engaged and the output was 307,000,000 pound.

In 1897 the Dingley tariff of 1.5 cents per pound on tin-plate was adopted and gave more protection to the industry. From that time, well into the twentieth century the American industry grew at a rapid rate and eventually the production equalled that of Britain.

CHAPTER 10

HOT GALVANIZING

10.1. GENERAL DEVELOPMENT OF THE PROCESS

10.1.1. Period of empirical working (Circa 1743 - 1836)

The first scientist to claim any degree of success with what is now known as hot dip galvanizing was a French chemist P.J. Malouin.

In a paper presented to the Academié Royale in Paris in 1743 (301) he described experiments in which he had made a similar product to 'white iron' as tin-plate was then called. Tin-plate manufacture had been established for many years and it would seem surprising that the well known preserving property of a zinc coat had not been exploited commercially before this time.

The reason for this can probably be attributed to the late development of zinc smelting which on investigation appears to have been achieved for the first time on a commercial scale as late as 1740.

Malouin who had many years' experience in hot dipping tin, claimed that the coating that was obtainable from dipping iron into a bath of molten zinc would last longer than a tin coat and would withstand higher temperatures without melting.

Interest in Malouin's discovery rippled through the scientific circles in Paris. The first application that sprang to mind was to use hot dip galvanizing to provide a cheap protective coat for household utensils. At this time hot dipping had been used to cover sheets with copper. These had been used to replace tin-plates which were too expensive for the

poor people. For a time this process continued to be used for covering domestic utensils.

In 1786 Bishop Richard Watson described a method (302) used in Rouen for zinc coating iron saucepans.

"The vessels are first made very bright so that not a black speck can be seen; they are then rubbed with a solution of sal-ammoniac, and afterwards dipped into an iron pot full of molten zinc".

For a time zinc appeared to provide the answer for a cheap substitute for tin.

In 1778, however, M. de la Folie (303) discovered that the zinc became corroded by organic acids. Zinc-plated kitchen utensils continued to be used, but after several years the 'death blow' came when it was realised that the salts formed on the zinc were poisonous.

Attempts were made to overcome these problems but none were forthcoming and interest in hot dipping waned.

In 1805 Sylvester in a British (305) pated stated:-

"Sheathed ships, roofed houses and lined water spouts with a certain material not hitherto used for that purpose". They also recommended the use of "nails coated with zinc to attach the zinc sheets to the ships sides or the surfaces". This expansion in the number of applications of the process gave it new life.

10.1.2. A time of scientific reasoning (Circa 1837 - 1838)

In 1837 M. Sorel took out in France, the first of numerous patents (SEE Ref 75) for a process of coating steel by dipping it in molten zinc and provided the process with its name 'galvanizing'. Fig. 85 illustrates the title page from Sorel's original patent.

Sorel used a pickling solution of 9 per cent sulphuric acid and the iron was pickled for about 12 hours. After dipping the iron in a solution of hydrochloric acid it was then dried in a store. Instead of fluxing with powdered resin as was done in the tinning industry he used ammonium chloride. After dipping, the articles were put in cold water, rubbed with sand and dried in sawdust. It is of note that Buschaendorf had used ammonium salts instead of tinners' resin as early as 1802.

A diagram showing the construction of the galvanizing bath designed by Sorel is shown in fig. 86.

AAAA represents refractory brickwork held together by strong steel bands.

BBBB is an iron bath resting upon a grid EE.

FFFF is a vertical space for receiving the fuel which burns in contact with the bath.

Ledru et Sorel

Métallurgie

Ministère du Commerce et des travaux publics.

Direction de l'administration industrielle et commerciale.

Bureau des Manufactures et de la statistique industrielle.

N° 1409.

Minute

Ch.

Add. 93.

10842/78

5601/

Brevets d'Invention,* de perfectionnement et d'importation,

établis par les Lois des 7 janvier et 25 mai 1791.

Certificat de demande d'un Brevet d'invention et perfectionnement de quinze ans délivré à MM. Ledru et Sorel, à Paris département de la Seine

Vu la Requête de MM Ledru (Hector) Négociant et Sorel (Stanislas) Ingénieur, demeurants à Paris, Rue du 29 Juillet N°6,

dans laquelle ils exposent que, désirant jouir des droits de propriété temporaire accordés et garantis aux auteurs et importateurs des découvertes et perfectionnements en tout genre d'industrie, ils demande un Brevet d'invention et perfectionnement de quinze ans, pour un moyen simple et nouveau de préserver le fer et l'acier de l'action de la rouille.

* Le Gouvernement, en accordant un Brevet d'Invention sans examen préalable, n'entend garantir en aucune manière ni la priorité, ni le mérite ni le succès d'une invention. (Article 2 de l'arrêté du Gouvernement du 5 vendémiaire an 9, 27 septembre 1800.)

FIG. 85 EXTRACT FROM SOREL'S ORIGINAL PATENT - THE TITLE PAGE No. 1409

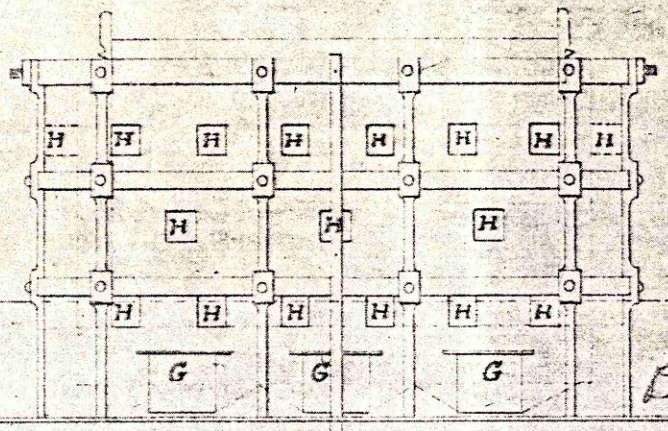
Légende explicative du fourneau et de son creuset

A A A A. maçonnerie du fourneau en briques réfractaires, liées avec de fortes bandes de fer B B B B. creuset en fer: a creuset repose sur la grille E E.

F F F F. gorge verticale pour recevoir le combustible qui brule en contact avec le creuset. H H. ouvertures latérales pour régler la combustion

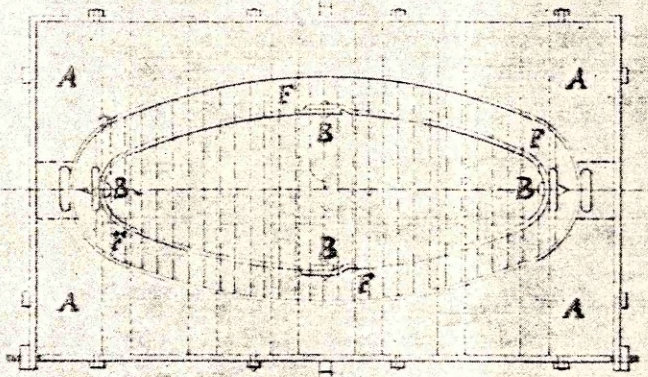
Sorel

Élévation



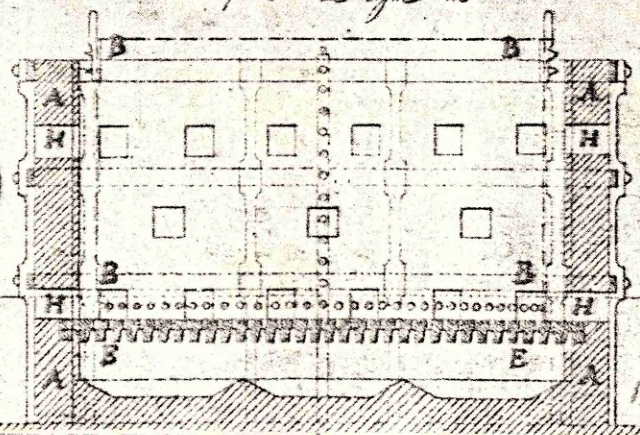
(5)

Plan



(6)

Coupe sur la ligne AB



(4)

FIG. 86 EXTRACT FROM SOREL'S ORIGINAL PATENT - SHOWING THE CONSTRUCTION OF THE GALVANIZING BATH

HH are side openings for regulating the combustion.

Sorel's contributions to the process, although important, have been magnified, especially by the French, beyond all proportions.

Sorel has been described as the "Father of the industry", and his work as the "birth of galvanizing".(306)

It will be recalled that Hobson, Sylvester and Moorhouse were galvanizing commercially as early as 1805.

In France between 1831 and 1838 many iron viaducts and bridges were built. Sorel, who was a civil engineer, probably realised the potential in the hot dipping process and through his experience as a practical engineer was able to make major contributions to the development of the process.

Up to 1837 developments had been by practical innovation rather than by scientific reasoning. Malouïn had earlier discovered hot galvanizing, but could not in any precise way explain the fundementals of the coating.

By 1837 the great developments of Galvani, Volta and H. Davy had taken place, and scientists were able to give expression to Sorel's work.

Shortly after Sorel's original patent, H.W. Crawford, a commander in the Royal Navy lodged a similar patent in England.(307)

According to the Mechanics Magazine of 1838(308) this came "following a communication from Sorel".

In this "improvement in the coating of Iron and Copper" he stated:-

"The coating which preserves iron and copper from oxydation is a coating of zinc .....The zinc may be used either in a state of fusion or in a solid state reduced into powder....".

10.1.3. Sorel's claim to originality questioned

A most interesting comment on Sorel's 'discovery' was made by

Robert Mallet, in the British Association Report 1838.(309)

".... I must remark upon the arrogation of original discovery to M. Sorel, the patentee of this process, which some French scientists make. It does seem strange how any pretension to originality of discovery can be now set up on this score, after the previous publications of Sir H. Davy etc. and still how a French patent is to be maintained for a process which, although its principle was doubtless then not understood was with little variation before patented earlier by Madam L. de Jancourt, for preserving metals from rust by covering with an alloy of zinc, bismuth and tin. I may add that Professor Davy informs me that he used the method of zincing over the surface of iron as early as 1834".

It is of note however that Prof. Davy was a close friend of Mallet and it may well be that this partly accounted for the marked lack of enthusiasm that Mallet showed for Sorel's contributions to the science.

10.1.4. Early galvanizing in Britain

Further comments on galvanizing in Britain in 1838 are recorded by Mallet:-(309)

"Very lately a company has now arisen in London, under the name of the British Galvanizing of Metals Company based on Sorel's patent. I lately wrote to the secretary of this company and have obtained specimens of the so called galvanized iron, which are now presented. I also wrote to another company styled the Zincked or Galvanized Iron Company, my letter was returned unopened".

In order to combat the discouraging comments that Mallet kept making on Sorel's contribution, the English, Scotch and Irish Galvanizing Company, submitted galvanized material to five distinguished British chemists, each one returned a

favourable report.(310) It is of note that after this experience Mallet's comments became more favourable although never enthusiastic.

The English, Scotch and Irish Galvanizing Company which had been formed in 1838(308) initially had premises in Southwark, London. In the following year the patent rights were transferred at a royalty of £3 per ton to the British Galvanizing of Metals Company .

The impetus for commercial development in Britain in 1838 had come from Sorel's work in France, initially, although Sorel himself had not been the inventor of the process. The industrial development in Britain and America was now progressing rapidly. Britain was now ahead of France in technical progress and the growth of the galvanizing industry consequently was faster here.

10.1.5. Interest shown by the Admiralty

An insight into the variety of applications that were being considered for galvanizing is given in the Report of the Committee on Metals to the British Admiralty, in 1846, on the uses of iron, section 7 - The best mode of preserving chain cables.(311)

"We have obtained information on the galvanizing of chain cables. A letter on this subject from Messrs. Morewood and Rogers, who have applied this process to chain cables for private individuals has been obtained. We have had sufficient experience of galvanizing to state that, under ordinary exposure to air and moisture, it prevents the oxidation of the iron. It also retards its destruction under all circumstances even when exposed to the action of sea water, but does not ultimately resist it". (Fig. 87).

At that time chain cables in store had been preserved with

COST OF GALVANISING CHAIN CABLES.

9, Steel-yard, Upper Thames-street, London,
Sir, 9 January 1816.

In reply to your letter of the 8th instant we beg to inform you that we have repeatedly galvanised chains, and can confidently recommend our process.

The following would be our charge for galvanising the same.

	£.	s.	d.	
1 in., $\frac{7}{8}$ in., $\frac{3}{4}$ in. -	11	–	–	per Ton.
$\frac{11}{16}$ in., $\frac{5}{8}$ in., $\frac{9}{16}$ in., $\frac{1}{2}$ in.	12	–	–	,,
$\frac{7}{16}$ in. - - -	14	–	–	,,

	£.	s.	d.	
$\frac{3}{8}$ in. - - -	14	5	–	per Ton.
$\frac{5}{16}$ in. - - -	16	5	–	,,
$\frac{1}{4}$ in. - - -	16	10	–	,,

We have, &c.
(signed) *Morewood & Rogers,*
Patentees of Galvanised Tinned Iron
Pro *Jno. Kincard.*

The Chairman of the
Committee on Metals, Admiralty.

FIG. 87 LETTER TO THE CHAIRMAN OF THE COMMITTEE ON METALS, ADMIRALTY (311)

black paint. The links of chains were found to wear by rubbing against each other particularly at their ends on the inside. Also the portion of the cable which was at the bottom of the chain cable was found to be more corroded than any other part. The Committee had doubts, and required (31) further information and tests, however they stated:-

"Upon the whole, therefore, in consequence chiefly of the increased expense, we are not prepared to recommend that the process of galvanizing be applied generally to chain cables; but we submit that a comparison be made for the sake of experiment, between the galvanized and ordinary chain by using them on different sides of the same ship, thus to prevent the contact of the two kinds in the same locker".

This was one application of galvanizing that was never entirely successful and even at the end of the nineteenth century the application of the process to chain preservation was unsatisfactory.

The objects, on which galvanizing was applied as a protective coat, became numerous and specialist industries were set up. The main applications however were for iron and steel materials which were to be exposed for lengths of time away from the sea.

10.1.6. Developments in Britain after 1850

By 1850 the U.K. industry used 10,000 tons of zinc each year. At the Crystal Palace exhibition of 1851 many galvanized articles were exhibited. When the Houses of Parliament were built in 1855 galvanized cast iron tiles were used for the roof of the Clock Tower housing of 'Big Ben'. It is of interest to note that when they were examined in the late 1940's the tiles were still coated with zinc.

An interesting series of experiments were carried out by Calvert[312] following a visit to one of the dockyards. He had found that the iron bolts which fastened the iron plates passed through the oak ribs and consequently would be prone to rusting.

His experiments consisted in driving through large pieces of oak, bolts and screws of unprepared iron and of galvanized iron and both sets were placed in soft and sea water for three months. The results showed that the zinc was not removed from the galvanized bolts due to the friction effects and also the oak and the galvanized bolts were unchanged. The unprepared iron bolts were rusted and the pieces of oak had become quite black.

During the latter part of the nineteenth century no spectacular new developments took place, but many of the existing techniques were gradually improved.

Quite separate from hot galvanizing, electrogalvanizing, a quite different process was making a considerable impact. This was only within a limited sphere of operation, which, in general, did not coincide with the main stream of application in which hot galvanizing had become firmly established.

10.1.7. Developments in Germany and France

Although there are reports of galvanizing plants having been started in Germany at Solingen in 1847. Thum[313] stated in 1876:-

"In Germany the general opinion on galvanizing has not been favourable; the employment of the process has been extremly limited and therefore almost unknown".

However by 1887 there is a report of experiments carried out on the use of zinc coated iron water pipes[314]:-

"As the result of a discussion at a recent meeting of the German Society of Gas and Water Engineers, experiments have

shown that the use of galvanized pipes should be in no way detrimental to health. Newly coated pipes give up zinc to the water flowing through them, but in quantities so small as to be perfectly harmless".

In general there was little interest in galvanizing during the nineteenth century in Germany and this has been confirmed by the German Zinc Development Association.(315)

After the great impetus that had come from France in 1837, the development of the process had been continued first in Britain, and also later in America. Partly due to instability that existed in France, and a slower pace of industrial development, the demand for galvanized materials was not as great as that in Britain. As a consequence, the growth of the industry was retarded in France compared with that in Britain.

10.2. SHEET GALVANIZING

Originally galvanizing was applied only to various iron articles and utensils of relatively limited dimensions; then gradually it was extended to the semi-fabricated products. Sheet galvanizing as a separate industry appears to have started in 1846 by Morewood and Rogers with the establishment of a rolling and galvanizing plant in Wolverhampton. Morewood and Rogers had previously had experience with hot dipping tin sheets. (SEE British pat, 1848/10,859)

From 1843 the galvanizing process had been applied to the production of flat sheets. The production of corrugated sheets was also being developed at this time, and several firms were established during the 1850's that both corrugated and galvanized sheets.(316)

Fig. 88 shows the Crown works at Wolverhampton. The galvanized corrugated sheets can be clearly seen.

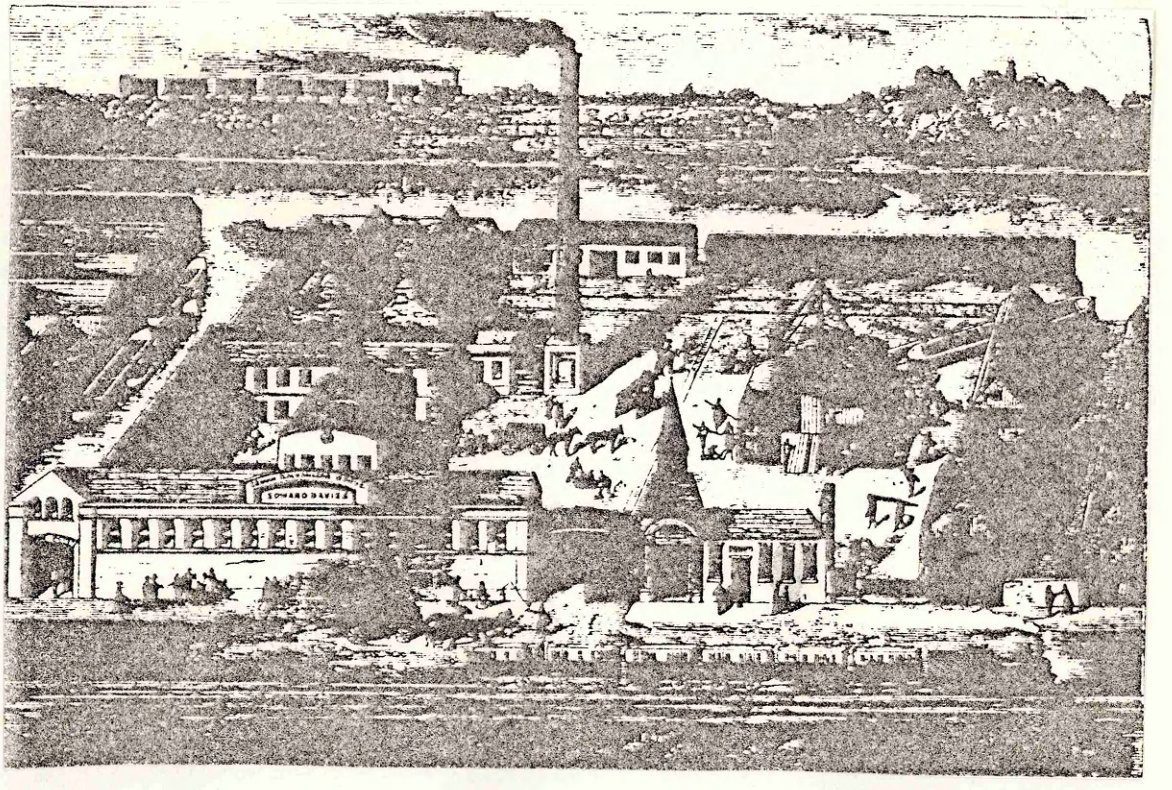


FIG. 88 DAVIES'S CROWN GALVANIZING WORKS

AT WOLVERHAMPTON

At the Crystal Palace Exhibition in 1851 models of portable buildings of galvanized sheet were shown. In 1852 the charge for galvanizing sheet was stated as within the range £6 - £18 per ton over the cost of black steel.(316)

10.2.1. Developments in Britain and America

The first attempts at sheet galvanizing were very crude, and consisted of literally dipping the sheets after pickling into a bath of molten spelter. This dipping was accomplished by hand. The bath or pot was large enough to receive the largest sheet it was proposed to galvanize and of sufficient depth to allow for the width of the sheet, plus a small clearance.(317)

At first the molten spelter was left entirely uncovered but this was found to be impractical because of the high oxidation rate. To prevent this the bath was covered with some material, such as sand or coke, but sheets coming through were as dull as if they had been coated with lead, and in addition carried a very irregular thickness of coating. This was overcome with the use of sal ammoniac. The sheets were placed on the edge of the pot by hand on the entering side and lowered through the flux and molten spelter on two or four hooks, the number depending on the length and weight of the sheet being treated. The dippers, as distinguished from the 'catchers' who were stationed on the exit side of the pot, pulled up on the hooks until the edge of the sheet showed above the flux. The catchers, who were provided with tongs having rivet heads for points and a rope attached to one of the handles, gripped the sheet. The ropes were run over a suitable 'pull-up' supported on an overhead shaft. By this means the men then pulled the sheets

up by hand and left them suspended for a sufficient length of time to set the spelter coating.

A crew of 12 were required to operate one of these long pots and consisted of two dippers, two catchers, two sawdusters who were boys, two inspectors and two picklers. The average output on the heavier gauge 12 to 24 was about 4 to 5 tons in 10½ hours. The crew worked double shifts.

After the spelter was set, the sheets were let down into water, the purpose being to remove the flux and 'kill' what remained, otherwise the spent flux would have sweated up and left white marks on the sheets. After inspection for flux spots and uncoated places, satisfactory sheets were branded with the makers name and trade mark. (317)

The wood engraving in fig. 89 represents Mr. Edward Davies' Crown Galvanizing Works. The brand of the Crown Works was a crown surmounting the Staffordshire knot.

FIG. 89 THE DAVIES BRAND FOR GALVANIZED SHEETS

In spite of the crudity and wastefulness, this method of galvanizing was in operation for many years.

About 1884 - 5, several attempts were made in the Wolverhampton district to emulate the mechanical handling carried out in tin-plating. (317) These attempts were comparative failures because of failure to take into account the comparative lengths of the sheet as compared with the tin-plate, since at this time

tin-plate never exceeded 20 inches in the longest dimension. The galvanizers provided only one pair of rolls on the exit side of the pot and these were too small in diameter. About 1886 John Tinn of Bristol experimented with rolls equal to the width of the sheet instead of the length, he shortened the pot and forced the sheets lengthwise through the spelter between curved flat bar iron guide (fig. 90). However he still used one pair of small diameter rolls on the surface of the metal on the exit side, with the result that as the sheets became heated by contact with the molten metal, they softened, and it was difficult to force them. Tinn found great difficulty with sheets longer than 6 ft. in 24 gauge and heavier, and anything lighter than 26 gauge. He had a great length of travel in the molten spelter without support and in order to shorten the travel he shortened the guides, with the result that the sheet was not long enough in the spelter to become the same temperature as the bath and consequently would not take the coating. This fact was not appreciated at the time since the hand practice was the only guide available and this was sufficiently slow for the sheet to reach the proper temperature.

This problem was eventually overcome by Clement Poppleton who had joined John Lysaght, one of John Tinns competitors in 1888.

It is of interest to mention at this stage that in fact the Kelly's Directory of Bristol for this period records that both Tinn's and Lysaght's premises were both located in the same lane - Silverthorne Lane, Bristol.(318)

10.2.2. Clement Poppleton's contributions

Clement Poppleton made a significant contribution to the development of the industry first in Britain and later in America.

He developed the first four-roll galvanizing machine, the second pair of rolls were driven and placed underneath the metal towards the bottom, leading the sheet into these rolls was by means of much shorter guides. From these submerged rolls the sheet passed to the exit rolls by means of these guides. This change was an improvement, but the difficulties were far from being entirely overcome.

The first need was for devising a means for driving the submerged rolls. A partial solution to this was the provision of a gear large enough to mesh with a gear on the neck of the top roll of the submerged pair and at the same time to mesh with a gear on the neck of the back roll of the exit gear. The most apparent fault of the big gear was found to be the excessive motion it gave in the pot, constantly bringing different particles of molten spelter into contact with the air, with the resultant excess of zinc ashes.(317) Poppleton was not able to remedy this for many years and it was a constant source of trouble to the dipper. He constantly had to dip flux onto the gears with a ladle, in spite of the danger of getting the flux between the exit rolls, for this would have resulted in spoiled sheets.

The next difficulty that Poppleton found was finding a material for the gear which would not be effected by the molten zinc. He tried first with cast iron gears, but at the end of a week's run the teeth were missing. He observed this when the sheets refused to travel, for when he lifted the frame from the machine it was found that the bottom rolls were not revolving. He next tried steel castings for both the small and large gears but they only lasted a day.(317)

The great advance came when a worm drive was substituted for the large gear. This modification also solved the zinc ash

problem, as the direction of rotation of the worm shaft was in the opposite direction to the upward throw of the large gear and as a consequence the spelter was hardly disturbed. Any slight disturbance did not bring the constant stream of molten spelter to the surface as was the case with the big gear. The material used for the worm and gears was hammered steel with cut teeth.

Problems arose in finding a suitable frame to carry the rolls and guides. Light frames were easy to handle but they soon warped to such an extent that the gears would not mesh and the rolls could not be kept in line.

After the first experiment, cast iron rolls were discarded in favour of rolled steel shafting which was made with a diameter of 8 inches. Rolls of 12 inches diameter were tried but were found to expose too much surface to oxidation, especially in the case of the exit rolls.

The material of English frames was 0.40 - 0.55 per cent carbon steel.

The drum was arranged with a series of points projecting about 3 inches above the drum so that the still unset spelter was not smudged and showed a uniform spangle. For the better grade of sheets the chain conveyor took the sheets into a washing tank, the function of this washing tank being to remove all the spent flux. The chain conveyor was of sufficient length to permit the spelter to set and spangle before reaching the washing tank. After washing the sheets passed through a "mangle" consisting of two pairs of finely finished rolls, the first pair being rubber covered to squeeze off the water, and then pass over a short furnace. Next the sheets passed through a second mangle having plain uncovered rolls. Three or four sheets at a time were gripped between jaws which extended the full width of the sheet. This operation left the

sheets perfectly flat.

10.2.3. Preparation of the sheets

In America a system of flattening was devised in which the sheets were passed through a series of many rolls, some machines having as many as 17 rolls. This system tended to be more automated but the results tended to be inferior to the English system.

In English works the sheets were dried before entering the pot. This saved the flux since the sheets were more nearly at the temperature of the flux box. This technique also lessened the tendency to 'blow', which wet sheets tend to do, so wasting both flux and spelter. The heating of the sheet also dries off the hydrogen left after pickling and considerably lessens the number of grey sheets.

About 1892 John Thompson of Wolverhampton, a manufacturer of galvanizing pots, received an order for two complete outfits of machines and pots for shipment to a sheet galvanizing firm in Philadelphia. This is believed to be the first installation of the four-roll galvanizing machine in America.

10.2.4. Controlling the coat thickness

A typical American machine is illustrated in fig. 91. Comparing these machines with an English galvanizing machine of this period, it can be seen that the inclined feed rolls over the flux box are in a vertical plane in the English machine, (see fig. 90).

Next in importance is the arrangement of the space to accommodate the roll necks of the front or exit rolls. Instead of this being open to the front, as in the English machine, the American machine, accommodated the necks of the exit rolls by dropping the forged frame. This added to the ease of

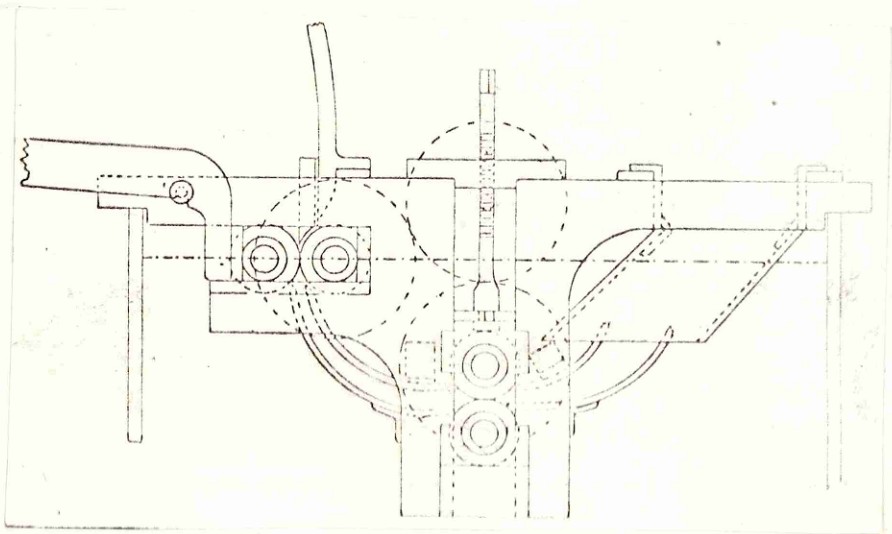


FIG. 90 SIDE VIEW OF AN ENGLISH GALVANIZING MACHINE SHOWING ROLL SCREWDOWN (317)

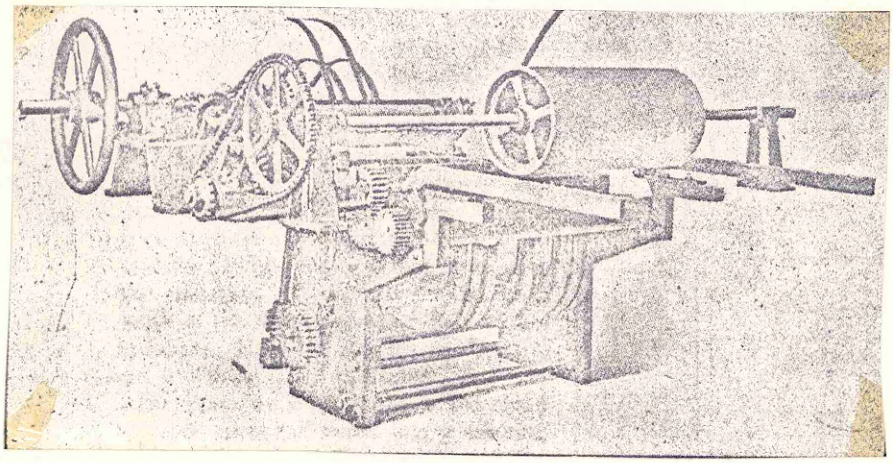
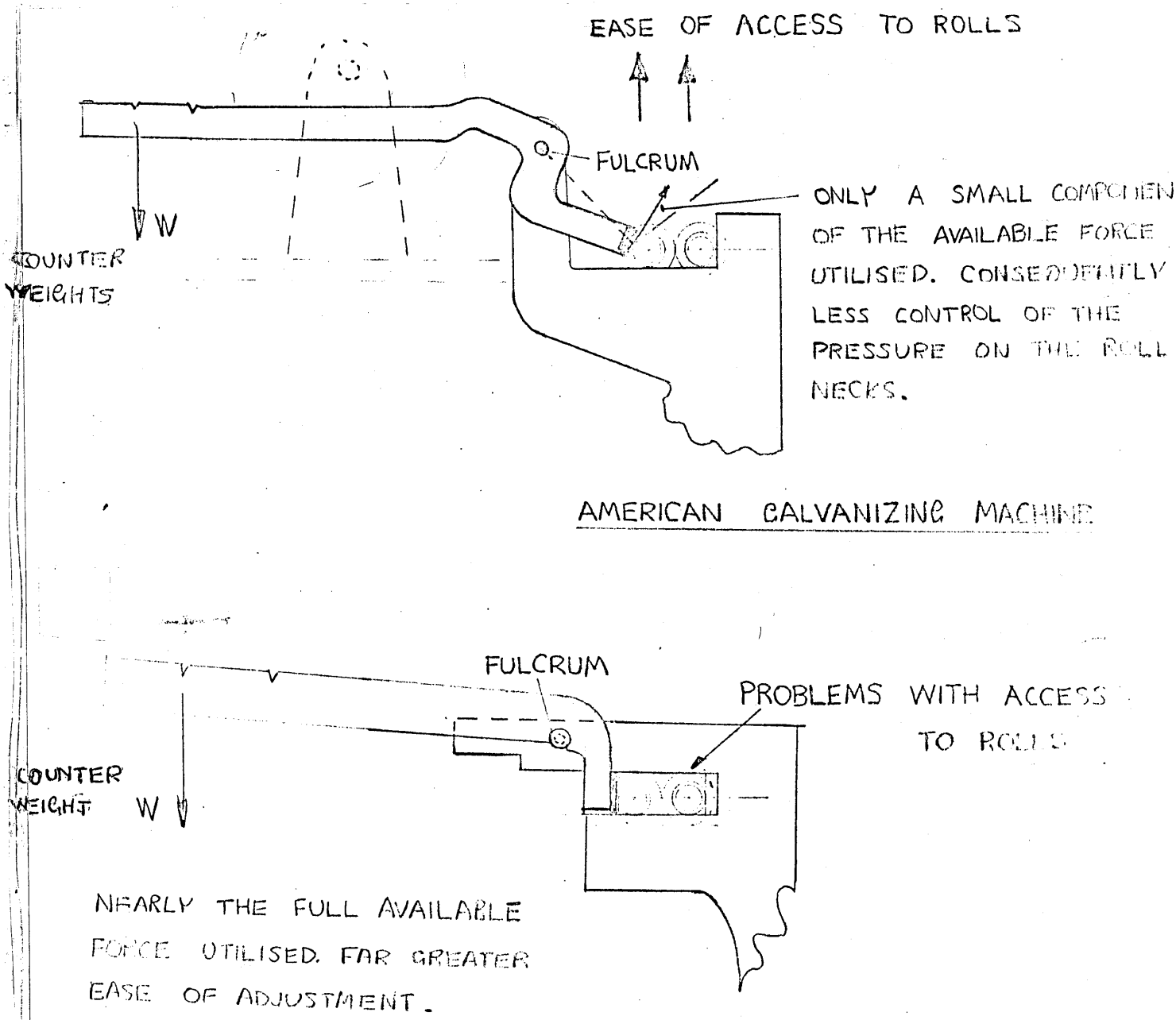


FIG. 91 VIEW OF A NINETEENTH CENTURY AMERICAN GALVANIZING MACHINE FROM THE DISCHARGE SIDE SHOWING THE METHOD OF DRIVING THE ROLLS

access to the rolls, but somewhat at the expense of ease of adjusting the pressure on the roll necks (fig. 92). This was an important feature, since the spelter yield depends upon this adjustment. The material used in the American machine was very similar to those used in the English design. The pressure on the necks of the top rolls was regulated by means of two levers, one on each side, the levers being provided with counter weights, (see fig. 92). The weights were necessary on account of the different thicknesses of sheets galvanized. There was no other major difference between the two machines except in the shape of the levers. The American machine had hammered steel rolls of 8 inches diameter. The top rolls were turned smooth and parallel with a shallow spiral groove cut in them. The English machine had its rolls left smooth. When the top rolls had worn down they were 'turned up' and used for bottom rolls. The top rolls were usually relegated to the bottom when they had been turned down to $7\frac{1}{2}$ inches diameter and this was found to occur after about 6 months service.

The main advantage of the American system was the worm drive. It was smoother running having practically no backlash when new and the wear was much less than with spur gears. Another advantage was that it was possible to run the top rolls slightly faster than the bottom ones, this was not possible with the English gear system. This reduced disturbance in the pot.

One of the problems found at this time both in America and England was the removal of parts due to the destructive action of the molten zinc spelter. Spur gears sometimes lasted for only about four weeks service and worm gears about eight weeks. Roll necks had to be renewed weekly.



THE CONTROL OF COAT THICKNESS WAS DEPENDENT UPON THE EASE OF PRESSURE ROLL ADJUSTMENT.

FIG. 92 AN ANALYSIS OF THE ROLL NECK MECHANISMS ON 19th CENTURY GALVANIZING MACHINES

To overcome this problem rolls were finish machined to 8 inches diameter on the barrel, with necks 2½ inches, and afterwards bushed up to 4¾ or 5 inches. These bushings were from forged steel bored to size and shrunk on. It was not of the same importance with the bottom rolls, because they did not have to run smoothly since they acted only as conveyors and did not influence the spelter yield.

10.2.5. Cooling the galvanized sheet

In England the sheets were washed after galvanizing but in America a cooling wheel was used extensively in conjunction with a conveyor and washing tank. In England only the highest grade material was treated in this way. Usually the sheets were taken from the exit rolls by hand and placed on the floor on edge until they were cool enough to be inspected. This inspection was accomplished by bending the sheets to a slight radius.

A modification to the preparation of iron and steel sheets prior to galvanizing was brought out in 1888 by a patent submitted by Davies Bros., of Wolverhampton. (319)

In this patent they passed the plates after pickling between cold rolls which were sprayed with water. In this way they improved the quality of the coat which after a pickle was pitted and uneven. The plates were then dipped in the normal way. (fig. 93).

10.2.6. Use of spelter

Commercial spelter consisted of about 94 per cent zinc, 2 to 2½ per cent tin and the remainder lead. On becoming molten in the pot the lead became stratified and on account of its greater specific gravity, fell to the bottom.

All metals are soluble in molten zinc, consequently the sheets

in their passage through the pot, the rolls and guides and frame, gave off iron in minute particles, which combined with the spelter in the pot to form what is known as 'dross'. Dross has a specific gravity between that of zinc and lead, consequently it floated on top of the lead and below the zinc. Dross was a major problem, since if there was any on the sheets it ruined them, and this at the least meant re-dipping drossy sheets.

Consequently the designer had to make sure that the pot was deep enough to allow the dross space to fall without interfering with the process. At the same time the sheet required to have a certain depth of travel under the spelter to have sufficient time for heat and also to allow a workable curve for the guides. This distance was found to be not less than 16 inches from the spelter line to the split of the bottom rolls, plus eight inches, the diameter of the rolls, plus one inch clearance above the dross.

The superintendent had to be careful not to allow the dross to rise above the safety limit. This was accomplished by sounding with a steel rod. When the danger zone was reached the machine had to be lifted and the pot removed of dross. This was usually carried out at weekends.

10.3. WIRE GALVANIZING

10.3.1. Introduction

Interest in wire galvanizing started about 1850 with the formation of the telegraph companies. Underground cables had been found to be too expensive to maintain and the method of aerial suspension was adopted. The wires were protected by the new galvanizing process, paint and tar having been discarded as expensive and ineffective. The process was also used for submarine telegraphy.

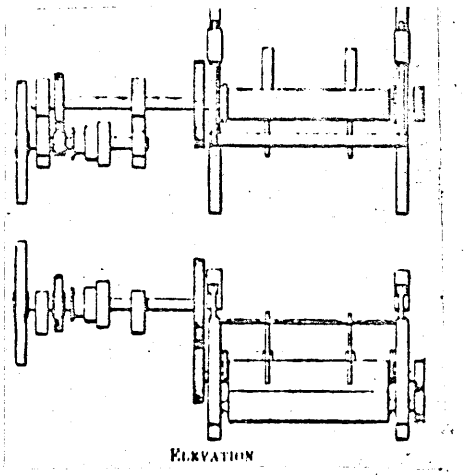


FIG. 93 APPARATUS FOR WET-ROLLING AFTER ANNEALING AND PICKING AS USED BY DAVIES BROS. OF WOLVERHAMPTON

10.3.2. Bedson's contribution

The first specialist equipment came from a patent by Bedson in 1860 on the continuous treatment of wire by "pickling, rinsing, fluxing and dipping".(320)

The machine invented by Bedson in fact made wire drawing the first specialised branch of the galvanizing industry. Wire making was carried out at Warrington, Manchester, Sheffield and Newport.(289)

The process, which was carried on both day and night, was basically similar to that of galvanizing sheets. In wire drawing however child and female labour was extensively used.

The wire galvanizing plant was almost always part of a wire manufacturing company, since the handling equipment required for continuous galvanizing was similar to that used in other stages of wire manufacture.

The process for galvanizing wire is basically similar although less complicated, than that for galvanizing sheets. The wire after being drawn was passed through a bath of zinc spelter. Boys were employed to watch the wire as it passed from the machine, through the zinc baths, and was wound on to blocks on the wheels.(321)

10.3.3. Problems with the reduction in wire strength

One of the problems with the hot galvanizing process was that due to the heat; the strength of the wire was reduced. even under the most favourable conditions, steel wire of high breaking strain had its hardness, and consequently its ultimate tensile strength and elongation, reduced by as much as from 5 to 10 per cent.

It was the practice because of these problems when coating

steel wire to keep the bath of molten zinc at as low a temperature as possible and to run the wire through at a high speed.

In some cases the wire on leaving the bath was wiped between asbestos rubbers, but steel treated in this way was found to have a lower resistance to corrosion. This was due to difficulty in regulating the thickness of the zinc coating, the result being that an iron-zinc alloy was formed on the surface of the iron and no true coating of zinc.(322)

This difficulty in regulating the coating was a major problem, the zinc coating was uneven and the increased weight was often a matter for consideration. The thickness could only be varied within narrow limits, the minimum weight of zinc being about $1\frac{1}{2}$ oz per sq foot, the maximum 3 oz, except when the molten zinc was raised above the most economical working temperature and the wire passed through these asbestos rubbers. The process of hot galvanizing was necessarily slow, because the time of passing the wire through the bath was fixed, due to the fact that the temperature of the iron must be raised to approximately that of the spelter. An optimum speed was found to be between 50 and 60 ft per minute. Fig. 94 shows a wire galvanizing plant.

10.3.4. Wire dipping and centrifuging

Towards the end of the nineteenth century, experiments were carried out dipping the coils or bundles of wire in baths of molten zinc, and then placing the coil in a centrifugal machine to remove the excess metal, but this was not very successful. With the development of the electro-galvanizing process,(322) by Cowper-Coles, which maintained a constant thickness of coat and normal temperature of operation, interest in this application of hot galvanizing waned.

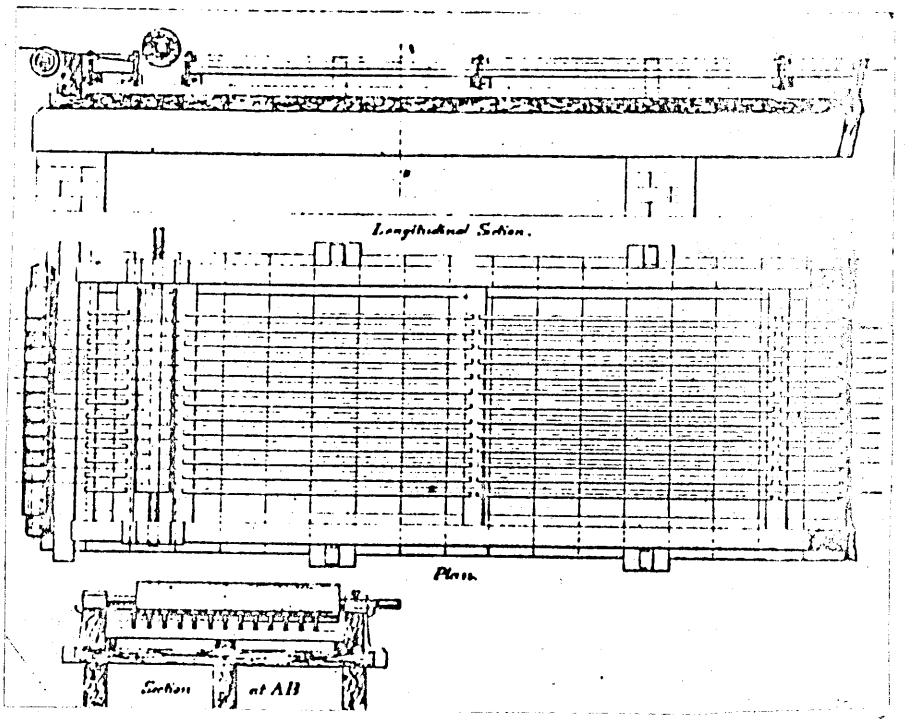


FIG. 94 WIRE GALVANIZING PLANT (322)

10.4. GROWTH OF A GALVANIZING COMPANY

The Crown Galvanizing Works had been founded in 1838 by Mr. Edward Davies. At the time of his death in May 1885, a report in The Engineer (323) stated;-

"The death is announced at the age of 69 of Mr. Edward Davies, one of the firm of Davies Brothers and Company, Crown Galvanized Iron Works, Wolverhampton. The deceased gentleman was one of the inventors of galvanized iron and introduced the manufacture into Wolverhampton".

10.4.1. Introduction of the process

The first record of his activities appeared in the Wolverhampton Post Office Directory for 1847.

"Davies, Edward brazier, tin-plate, zinc and galvanized iron work".

At this time he appears to have been involved in galvanizing in a small way. Sheet galvanizing as a separate industry had only been introduced by Morewood and Rogers the previous year. Although at this time Davies had been galvanizing for nine years, like many of his competitors had probably confined himself to small objects in limited quantities and so was able to carry out the other processes as well.

10.4.2. Necessity of specialisation

As the market for semi-fabricated and corrugated galvanized articles grew, with the Morewood and Rogers developments, the industry became more specialised as well as lucrative. Consequently, Davies and the other galvanizers, had to introduce mechanised equipment to keep in the market.

In Melvilles and Co's Directory of Wolverhampton for 1851 it stated;-

"Davies Edward tin-plate and zinc worker" and in the Trades

Directory of Wolverhampton 1862/3

"Davies Edward, galvanized iron worker".

10.4.3. Buildings gutted by fire

In the Wolverhampton Chronicle, Sept. 24th 1879, there is a report of a fire which partly destroyed the company premises:-

"Between nine and ten o'clock on Tuesday evening a fire broke out in the stoving and pattern makers adjoining compartments of the Crown Galvanizing Works (Messrs. Davies Brothers and Co.) Cannock Road. The frame of the shops being woodwork, and a room above being extensively fitted with shelving, the flames spread with great velocity.....

.....The fire brigade under Major Hay, were soon on the spot and there being no hope of saving the premises, then in flames, exertions were directed to prevent the spread of the fire, and there being an abundent supply of water from the adjoining canal, and the more substantial construction of the premises favouring it, the main building was saved. The total loss in structure and goods is between £1,200 and £1,500 which is only partially covered in insurance. The origin of the fire is unknown".

The works are illustrated in fig. 88.

The canal mentioned in the report is still in existence today although hardly used, but at that time it was used for transporting the corrugated sheet.

10.4.4. Formation of a limited company

By this time a partnership had been formed between Messrs. William and James Davies, which continued under the name of Davies Brothers and Company until the 7th March 1885 when a limited Company was formed which is in existence to this day.

The date that the founder left the company is difficult to trace since the records before 1885 have been lost.

However he died three months after the firm became a limited company. This might possibly have some significance. Over the years the company continued to be in the forefront and developed new techniques. A typical improvement being a patent[319] already referred to, taken out in November 1888, for preparing iron and steel sheets prior to galvanizing. Members of the Davies family are associated with the company at the present time.

10.5. PROBLEMS WITH THE COUNCILS OVER WASTE PICKLE DISPOSAL

As the volume of galvanizing increased towards the end of the nineteenth century, local authorities became concerned about the disposal of waste pickle from the plants.

In 1889,[324] Messrs Ash and Lacy applied to the Corporation of West Bromwich for permission to dispose of the pickle into the sewage, but the Corporation Sewage Committee considered that in the raw state it would corrode the iron sewers. The company suggested that prior treatment with limestone would be sufficient but the Committee considered that this would only partly neutralise the acid.

They decided therefore that the Company should not connect up to the sewer, but that they should send a sample to an eminent scientist who would then advise the council. It was doubtful whether the company pursued the matter at all, since nothing further was recorded about the incident. Some companies did battle with the local authorities on this matter. During the 1890's John Lysaght and Company were involved in a pollution case with Wolverhampton Corporation. The case concerned pollution of the Smestow Brook with waste galvanizing pickle. An account, extending to some 60 pages, of the correspondence and resulting enquiry is in the Council Minutes for 1896/7.

The result of the case was that Lysaght's moved their galvanizing works from Wolverhampton to Newport, Mon.

CHAPTER 11

ELECTROPLATING

11.1 EARLY DEVELOPMENTS CIRCA (1800-1836)

11.1.1 Development of the battery

The history of the process of electro plating, in its scientific though not in its practical application, dates back to Volta's discovery of 'chemical electricity' in 1799. Nine years earlier, Luigi Galvani had noticed that muscular contraction resulted from interposing a metallic conductor between a muscle and a nerve, but it was Volta who crowned his researches into the nature of Galvani's discovery of 'Galvanism' by producing a silver-zinc primary cell(75).

Volta, in producing the first Voltaic pile of zinc, gave to chemistry a very important instrument for research.

This instrument is illustrated in fig. 95. It consisted of a series of about twenty pair of plates of 'a' zinc and 'b' silver piled upon each other in regular succession, with a piece of card or flannel soaked in saline or acid solution separating each pair. It was found that the effects of this combination were much more powerful than those of a single pair of plates. When wires were connected to the ends of the instrument and plunged into water, minute bubbles of gas emerged.

The arrangement of the elements however was inconvenient, and Volta contrived another arrangement. This is illustrated in fig.96. An equal number of bars of zinc 'a' and silver 'b' were bent and soldered end to end and arranged so that while the zinc bar rested in one of the vessels, the slip of silver soldered to it hung in the other. Although an improved source of current was available from this cell, the current unfortunately diminished during continued operation and so the cell was not suitable for an industrial application.

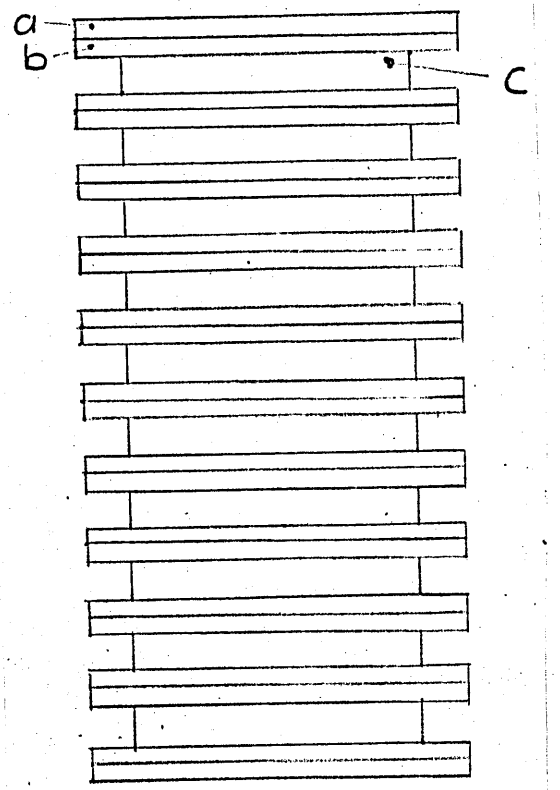


FIG 95 VOLTA'S PILE (75)

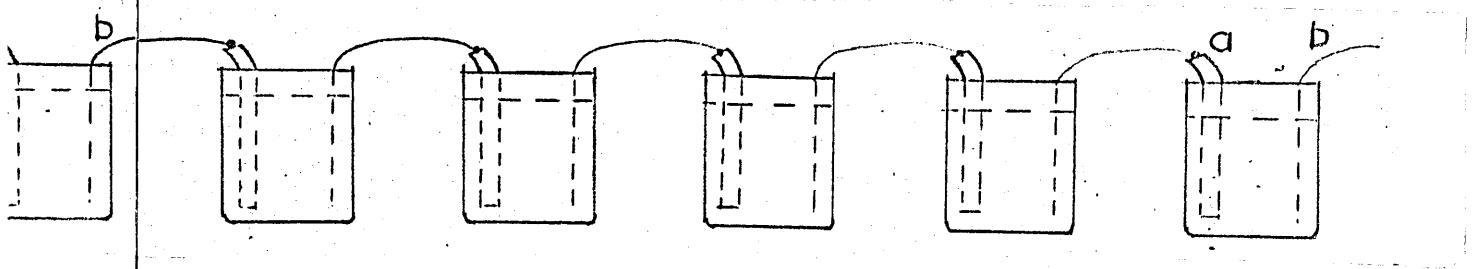


FIG 96 VOLTA'S EARLY FORM OF 'VOLTAIC' BATTERY (75)

11.1.2 Earliest record of electro-deposition

The first record of the electro-deposition of metals was described by Nicholson and Carlisle in 1800:-(325)

"A deposition of copper was formed at the lower end of the wire and at the end of four hours it formed a ratified vegetation nine or ten times the bulk of the wire it surrounded".

For details of the batteries which developed from this impetus SEE Ref. 326.

Significant results of a distinctly practical kind were nevertheless achieved during the early nineteenth century. Brugnatelli(84) gilded two large silver medals by bringing them into contact with the negative pole of a voltaic pile and keeping them immersed in a solution of ammoniuret of gold. In 1807 Davy made a further considerable advance in the science of electro-metallurgy when he decomposed potassium hydroxide and sodium hydroxide by using a powerful electric current from a battery consisting of 274 cells through fragments of moistened potash and soda, and deposited metal potassium and sodium metals upon the negative platinum wire.

Interest was sustained in electro-metallurgy at this time, not only by these striking results, but by the increasing speculation as to the relationship between electrical and chemical energy. A high peak in the more fundamental work was thus stimulated by Faraday's(327) discovery in 1833 of the fundamental laws relating the amount of current to the amount of metal deposited. This was to have a major influence in the direction of all subsequent scientific thought, and to become of basic importance in the development of the electroplating industry.

It was also during this period of electromagnetic induction, which later culminated in Faraday's discovery of the principles of the dynamo, that the foundation was laid of practical electro-deposition. This development, however, was to be delayed for some time and the lines of investigation, already mentioned that were pursued in improving Volta's cell, were to prove of more immediate importance.

It is interesting to note that whereas the development of the dynamo from Faraday's originial laboratory model was largely a matter of engineering progress, the engineer's method of approach in improving the Voltaic cell was less successful. Many modifications in design and construction involving shape and size of the zinc and copper led to no basic improvement in securing maintenance of a steady current output for a prolonged period of time. This only became possible after further investigation which established the fact that the chief cause of the 'falling off' of the current during use was the accumulation of a layer of hydrogen at the surface of the copper plate. Once this basic fact was established, methods for the effective removal of the hydrogen were devised. Smee[328] solved the problem by promoting the rapid discharge of hydrogen by coating the pole with platinum black. This is still used as one method of securing hydrogen depolarisation.

11.1.3 First useful battery for electrodeposition

Daniell adopted the principle of making the cathode process in the cell the deposition of copper instead of the discharge of hydrogen. It was this cell which provided the immediate stimulus that started industrial developments in the electrodeposition of metals. The cell itself not only provided a steady current but demonstrated the procticability of continuous deposition of copper. He called the cell the 'constant battery'. The principle of the instrument is that by placing copper sulphate in contact with the copper electrode, the hydrogen forms a combination with oxygen, copper is deposited and sulphuric acid formed.

A single cell is shown in fig. 97. It consists of an outer cylindrical copper vessel 'a'; in this cylinder is placed another cylindrical vessel of porous or unglazed earthenware 'b' and in this porous vessel was suspended a rod of amalgamated zinc 'c'; dilute sulphuric acid was placed in the interior of the porous vessel, and a saturated solution of copper sulphate in the exterior.

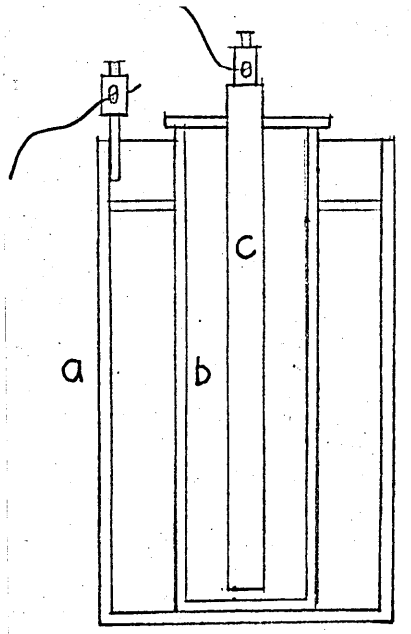


FIG. 97 DANIELL'S BATTERY (328)

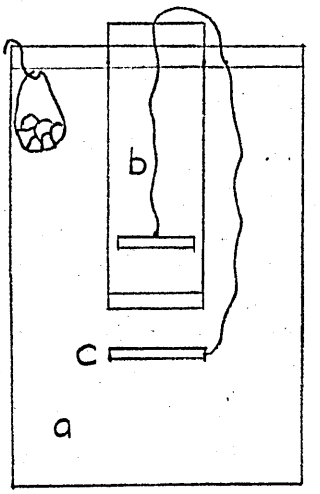


FIG. 98 SPENCERS' APPARATUS FOR PROCURING FAC SIMILES OF COINS AND MEDALS. (88)

When it was properly maintained, workmen found little trouble using the Daniell battery. If the cell was worked by strong acidulated water, greater attention was required, but when gilding was being done a weak current only was required and the zinc pot was charged with water only. The result was that after a few hours work, zinc sulphate was formed and this was found to have a favourable influence, enabling the battery to be operated without attention for many months.

In 1831, Bessemer coated articles composed of an alloy of lead, tin, iron and antimony with a film of copper by simple immersion in a solution of a copper salt, but he found that the metal was not adherent.

11.1.4. Faraday's significant discovery

In the same year Faraday showed that electricity could be generated by moving a coil of wire in a magnetic field. Quite sepqrate from the development of electroplating, many types of electrical generators soon followed. For details of some of the early generators SEE refs. 329, 330, 331

11.2 COMMENCEMENT OF INDUSTRIAL APPLICATIONS (CIRCA 1836-1852)

11.2.1. Discovery of Electrotyping

At this time however, in 1836, there was no direct relation established between the evolvement of deposition and that of magneto-electric machines. It was the development in the use of the Daniell cell that was to lead to the next important discovery, i.e. electrotyping and electroforming.

In Phil. Mag for 1836 De la Rue stated that the copper plate of his cell:-(85) "was covered by a coat of metallic copper, so perfect that being stripped off, it has the counterpart of every scratch of the plate on which it is deposited".

It was not the discovery of reproducibility that was important, since Daniell had noted from his battery that "it exhibited impressions of marks with extreme fidelity", but the emphasis that De la Rue placed on this discovery.

Daniell casually noticed these accurate reproductions, but did not consider this application for any useful purpose.

Within two years of De la Rue's observations being made, Jacobi of St. Petersburg, Jordon of London, Spencer of Liverpool and others were claiming priority for the discovery. It is probable that they were all independently following up the observations of De la Rue. The records show that the first published announcement was made on behalf of Professor Jacobi by M. Fuss[332] at St. Petersburg in October 1838, i.e. that:-

"a discovery of importance to copper plate engraving had been made by Professor Jacobi and the Empress of Russia had made funds available for further work".

Moritz Herman Von Jacobi was of German descent and a passing reference in Werner Von Siemens'[333] autobiography makes no reference to this disputation about the priority for this discovery:-

"In Autumn of 1840 I was transferred to Wittenberg, where I had to enjoy for a year the dubious pleasures of life in a small garrison town. All the more eagerly did I continue my scientific studies. In that year Jacobi's discovery was made known in Germany, the precipitation of copper in a metallic form by means of the galvanic current from a solution of the sulphate".

Jacobi gave the process the name of Volta-Plastics. Later, on May 4 1839, he made the announcement in England in the Athenian.[86] Immediately this was made known, Spencer, of Liverpool, announced that he had copied medals by the same basic method and he termed the process electrotyping.

Spencer's first communication to the public was on the 12th of September 1839[88]. In his address he gave details of the circumstances which led him to this application of 'Voltaic' electricity.

He stated:-

"..... when about to make an experiment, I had not a piece of copper available to form the negative end of my arrangement, and, as a good

substitute, I took a penny, and fastened it to one end of the wire, and put it in connection with a piece of zinc in the apparatus. Voltaic action took place, and the copper coin became covered with a deposition of copper in crystalline form. But when about to make another experiment, and being desirous of using the piece of wire used in the first instance, I pulled it off the coin to which it was attached. In doing so a piece of the deposited copper came off with it. On examining the under portion of which, I found it contained an exact mould of a part of the head and letters of the coin, as smooth and sharp in every respect as the original on which it was deposited". (Fig. 98).

In the diagram 'a' is a glass or earthen vessel, containing a saturated solution of copper sulphate, 'b' is a glass cylinder which was closed by means of plaster of Paris. This vessel contained a solution of sodium sulphate. 'c' represented the plate or mould on which the deposit of metallic copper was plated. A wire was fixed (usually by soldering) to this mould and was connected to a piece of zinc placed in salt water within the glass cylinder 'b'. To set the apparatus in action, Spencer filled the outer vessel with copper sulphate, and suspended some copper sulphate crystals either on a perforated metallic shelf or in a piece of muslin, to keep the solution saturated. The mould was found to become almost instantly covered with a layer of copper which increased in thickness so long as the strength of the cupric solution was maintained.

11.2.2 Rival claimants

A prolonged controversy raged for many years. In a letter to The Times nearly twenty years later, the Editor of the Journal of the Society of Arts stated:- (Fig. 99)

"The invention, as is well known, is a vexed question, at least four persons have appeared as claimants for the honour, of whom Mr. Spencer is one, the other three being Professor Jacobi of Russia, Mr. Jordon and Mr. Wright".

THE INVENTION OF ELECTRO-PLATING.

TO THE EDITOR OF THE TIMES.

Sir,—In your impression of the 5th inst. a memoir of the late Mr George Richards Elkington appeared, quoted from the *Journal of the Society of Arts*, but with the heading, "The Inventor of Electro-plate," a heading which does not appear in that publication. In your impression of to-day there is another paragraph with a similar heading, in which these words occur :—

"In the paragraph under this heading, taken from the *Journal of the Society of Arts*, which appeared in our impression of Tuesday last, the late Mr. Elkington was described as the 'inventor' of the process of electro-plating."

This statement is erroneous, as the paragraph in question makes no allusion to the invention of electro-plating, but merely describes Mr. Elkington as the "patentee" of the process in this country.

The invention, as is well known, is a vexed question; at least four persons have appeared as claimants for the honour, of whom Mr. Spencer is one, the other three being Professor Jacobi of Russia, Mr. Jordan, and Mr. Wright.

I am, Sir, your obedient servant,

THE EDITOR OF THE *JOURNAL OF THE SOCIETY OF ARTS.*

Society of Arts, Manufactures, and Commerce, Adelphi, W.C., Dec. 7. 1865

FIG. 99 LETTER TO THE TIMES ON DEC. 7th 1865 WHICH RE-OPENED THE CONTROVERSY WHICH HAD RAGED 30 YEARS PREVIOUSLY. (ELK. REC.)

"THE INVENTION OF ELECTRO-PLATING."

TO THE EDITOR OF THE TIMES.

Sir,—In reference to a letter from the Editor of the *Journal of the Society of Arts*, which appears headed as above in your impression of to-day, I trust you will kindly permit me to state that in my letter, to which you referred yesterday, I found little or no fault with the paragraph you quoted from the society's journal, but that it was to its heading only I objected, and which, as it now appears, was not his. His letter, however, informs me of the existence of another claimant to the discovery in question, in the person of a Mr. Wright, of whom, I assure you, I now hear for the first time. To this, however, I have only to say that the claims of the Russian Professor Jacobi, who is also named by your correspondent, were the only ones of which it was thought incumbent on me to take any serious notice, and that I have already had to deal with them in the presence of the professor himself, at a crowded meeting held in the University of Glasgow in 1840, and which was presided over by the late Dr. Thomson, Regius Professor of Chymistry, in the same University. At that meeting my independent right and priority were fully acknowledged, though I suppose, from what your correspondent says, I shall have to go over the ground once more, though as no one worth while refuting has ever since called my right in question, I have really not considered it incumbent on me to thrust myself or claims gratuitously before the public, which as a rule cares more for the practical results of a discovery than it does for the author.

However, as the subject has assumed its present shape, and as the Editor of the *Journal of the Society of Arts* is an authority one might be justified in taking some trouble to set right, I shall esteem it as a great kindness on your part if you will permit me to say in *The Times* of to-morrow that in the course of a week or two I shall republish such evidence as shall, I trust, leave no room for any to say with this gentleman that the question remains a "vexed one."

Very respectfully yours,

Euston-square, Dec. 8. THOMAS SPENCER.

FIG. 100 LETTER TO THE TIMES ON DEC. 8th 1865:- THOMAS SPENCER PRESSES HIS CLAIM. (ELK. REC.)

THE INVENTION OF ELECTRO-PLATING.

TO THE EDITOR OF THE TIMES.

Sir,—Seeing in your paper of Saturday last a letter from a Mr. Spencer claiming to be the inventor of electro-plating, I shall feel obliged if you will favour me with space to inform him and the public that I claim for my brother, the late Mr. John Wright, surgeon, of Birmingham, the honour of being the inventor of that process.

Mr. Wright made an arrangement with the Messrs. Elkington for the patent, to be taken out by Mr. Henry Elkington, which he did in December, 1837, agreeing to pay Mr. Wright 1s. per ounce for every ounce of silver or gold deposited by his process. This my brother received till his death in 1844.

After which his widow made another agreement with Mr. Elkington, to pay her a handsome annuity for her life. She is still living, and is receiving the benefit of her husband's valuable discovery.

I never heard of Mr. Spencer or any one else disputing the patent with Mr. Elkington, or yet claiming any royalty.

I am, Sir, yours very respectfully,

32, Bucklersbury, London, Dec. 12. W. WRIGHT.

*** We can insert no more letters on this subject.

FIG. 101 W. WRIGHT'S CLAIM ON BEHALF OF HIS DECEASED BROTHER. (ELK. REC.)

The letter brought an immediate response from Spencer, fig. 100, in which he completely dismissed Wright and stated:-

"..... the claims of the Russian Professor Jacobi, were the only ones of which it was thought incumbent on me to take any serious notice, and that I have already had to deal with them in the presence of the Professor himself at a crowded meeting held in the University of Glasgow in 1840, and which was presided over by the late Dr. Thomson, Regius Professor of Chemistry. At that meeting my independent right and priority were fully acknowledged ..."

There were no further comments in The Times from anybody that had attended that 'crowded meeting' and so Spencer appeared to have 'an independent right and priority' over Jacobi. (86)

There was however a response from Wright's brother in The Times shortly afterwards:-(fig. 100)

".... I claim for my brother, the late Mr. John Wright, surgeon, of Birmingham the honour of being the inventor of that process ...." (SEE II.2.6)

This claim, however, was completely out of context and would probably never have been made by Wright himself.

J. Wright could certainly claim to be the initiator of practical electrodeposition, but he was never directly involved in his work at Elkingtons with electrotyping at the time of its inception.

W. Wright's letter of December 12th in which he stated:-

"....Mr Wright made an arrangement with Messr's Elkington for the patent to be taken out by Mr. H. Elkington, which he did in December 1837 ...."

is distinctly misleading, since Wright's association with the Elkingtons occurred by a chance meeting in 1840.(91) After this letter the editor of the Times declared the correspondence on this subject closed.

It is difficult to determine the question of real priority between the inventors. Jacobi seems to have been the first to publish an account of his researches, Spencer next declared his intentions to describe his experiments; but was forestalled by Jordan. On the other hand Spencer claims

to have been the earliest experimentor in the field, and his investigations appear to have been deeper and far more fully developed than those of either Jacobi or Jordan. It appears to be one of those frequently recurring instances, where the progress of knowledge has led several men to a simultaneous but independent development of the same line of thought.

11.2.3 First Electroplating Patent

At the time that Spencer was engaged in electrotyping copper in Liverpool, George and Henry Elkington were engaged in coating military and other ornaments with gold and silver in Birmingham.

The method they used was that of simple immersion in hot solutions of those metals. This process was patented in 1836.(334) At about this period Mr. Elkington moved his business from St. Paul's Square to more convenient premises in Newhall St. Birmingham (335) (fig. 102.)

Two further patents for coating metals were secured by Mr. Henry Elkington, on February 17th (336) and December 4th (337) in the following year.

No mention is made in any of these patents of the deposition of metals by the use of electricity, but in the patent granted July 24th 1838 to Mr. G.R. Elkington and O.W. Barrett, (338) in the specification it is explained that the process of "coating metals is by the immersion of the metal in the solution of zinc in contact with zinc" and this patent is classed in a book published by the Authority of the Commissioners of Patents among "specification relating to electricity and magnetism, their generations and application". A foot-note explains:- "Although no mention is made of electricity in the specification, the immersion of the metal in the solution of zinc, in contact with zinc, or the amalgam of zinc forms a galvanic circuit thus employing electric force". This was the first electroplating patent.

In connection with this patent, there is an agreement dated 23rd November 1838 between Barratt and G.R. Elkington in which Barratt devises to Elkington his share or claim in the invention. (335)

8 Waterloo st May 15. 1836

Messrs.

Three Parties only are Estimating for the Works in Newhall st namely Mr Matthews Mr Buckler & James Davis Barr Potts declining to Estimate I have herewith sent you I have requested Buckler & Davis to take an Estimate from Mr Richards for the Stone Work & delivered the Estimates & Tenders to be delivered into Mr Hardaman Paradise st on or before 10 o Clock on Friday morning I have herewith enclosed you a Plan of Mr Wheelers Property. The Rental asked is 280£. The lowest Sum which Mr D Houghton says will be taken is 250£ This includes every thing on it now in except furniture. Please to return the Plans to morrow Untill then you have the refusal I have had two applications for your Premises but when informed the Parties that the Property was in Birmingham Parish they did not seek to make further enquiries Please to inform me of which & send the Plans & Specification to any one else Etc Etc Yours Messrs

Yours most faithfully

FIG. 102 ESTIMATES FOR BUILDING ELKINGTON'S NEW PREMISES IN NEWALL STREET, BIRMINGHAM 1836. (ELK. REC.)

Fig. 103 is a record of the goods sold by the Elkingtons during 1838.

Fig. 104 is a receipt for contract work during the same year.

11.2.4 Electroplating zinc in Europe

The industrial processes concerned with silver, gold and various other deposits had not been applied to zinc.

Sorel was one of the first to carry out practical studies on the electrolytic process for zinc. In December 1840 he presented a paper to the Academy of Science in Paris[339] on his patent:-

"there is the possibility of a new method based on Daniell's electrochemical method of a constant flow of electicity resulting in a layer of zinc being deposited on the iron. Iron galvanized cold in this way was completely protected from oxidation. The zinc adheres much better than that tinned by means of a molten bath dip".

The following year M. Dumas[340] made known to the Academy the work carried out by Elkington, Ruolz and others:-

"M. Ruolz has succeeded in finding an economic method to galvanize iron and steel by means of a battery which dissolves the zinc by a cold operating method and consequently maintains the strength of the metal to the smallest detail. Thin layers are applied which retain the general shape and appearance to the smallest detail. A thin sheet which receives this treatment is unlikely to become brittle and so the method can be used on sheets and become a very cheap way for roofing buildings".

About this time in Belgium M. Louyet experimented with both alkaline and neutral baths. He concentrated on neutral baths with a solution maintained at about 22-25°C in a wooden vat. The objects were placed in the baths for 30 minutes at the most and M.Louyet recommended that the anodes should be shaped similarly to these objects and that agitation should take place.

Two years later Louyet[341] made known the results which he had obtained and the conclusions which he drew were of considerable interest.

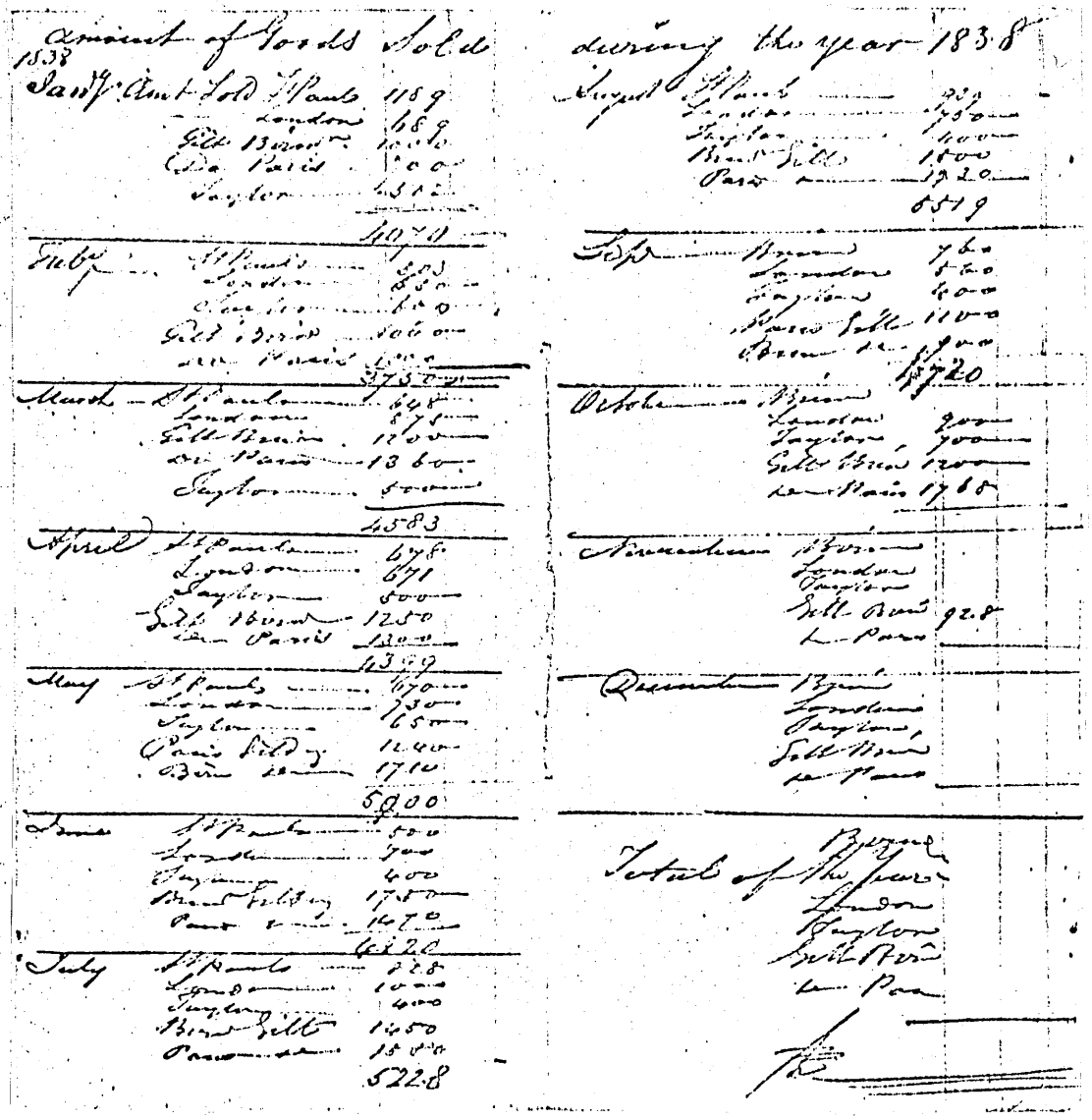
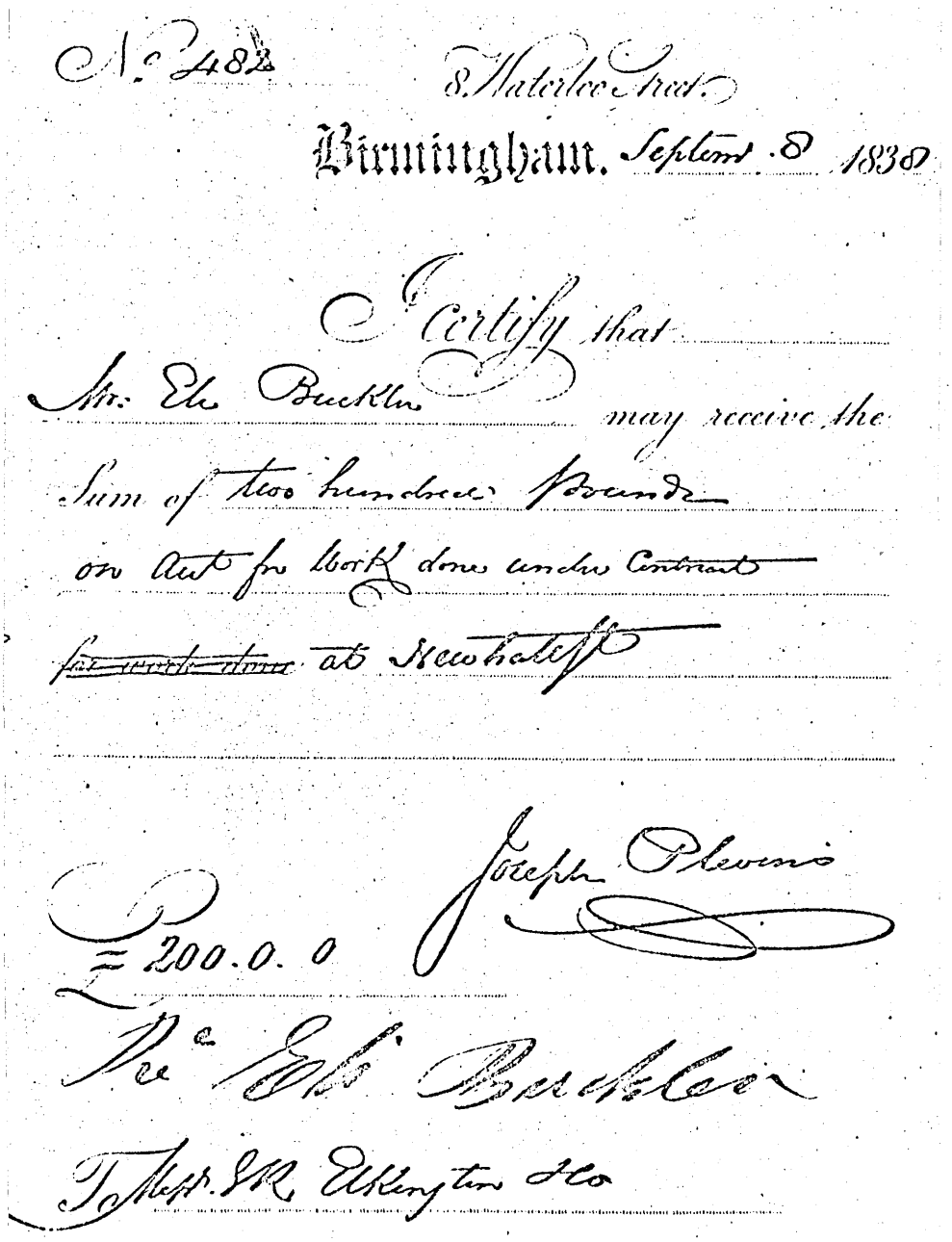


FIG. 103 GOODS SOLD BY MESSRS. ELKINGTON DURING 1838 (ELK. REC.)



No 2482 S. Waterloo Street

Birmingham. Septemr 8 1838

I Certify that

Mr. Eli Bucklin may receive the

Sum of two hundred Pounds

on Acct for Work done under Contract

~~for work done~~ at Newtakeff

£200.0.0 Joseph Plevins

Per Eli Bucklin

To Messrs. R. Elkington & Co

FIG. 104 RECEIPT FOR CONTRACT WORK 1838 (ELK. REC.)

In the first place he maintained that the deposits produced by him in the neutral baths did not have the resistance to tests in service and did not present the protection against rust which had been generally assumed. He had then abandoned these baths and (341) experimented in acid baths recommended by Pellatt. He obtained excellent results only when using much reduced voltages.

In his view the success did not result from greater conductivity of the bath but that the acid destroyed the oxide film on the surface of the iron.

The bath used was composed of zinc salts with a very small addition of sulphuric acid, the temperature being 22°C and the duration of the operation 13-36 minutes for thicker deposits. He remarked that when the bath had been used several times it gave better results.

11.2.5 Description of Electroplating process

In the electro galvanizing process of zincing, the work is the cathode and the anodes are made from commercially pure zinc. The anodes must be clean, of good quality and also because of the special shapes in which they are cast, they cost more than spelter. The residues of the process are a greyish powder which falls to the bottom of the vat. Over the years many solutions have been used, a typical one being a zinc sulphate solution.

The articles to be treated by this process are first thoroughly cleaned of scale, rust and grease by an acid pickle, sand blasting or some other method and placed in the solution. A low voltage is then applied to the system and zinc is deposited from the solution upon the articles.

While the major interest in electro galvanizing zinc centred in France in 1840, electrodepositors in England were bubbling with excitement over new discoveries that were regularly taking place in electrodepositing copper, gold and silver.

11.2.6. Wright discovers benefit of cyanide bath

At this time other types of plating had been in existence for many years.

The first substitute for silver had been 'Sheffield plate', originally sold at half the price of silver. Sheets of standard silver and copper had been rolled together causing the metals to fuse together. After rolling to the required thickness, they were stamped or spun to the desired form. The application of Sheffield plate had the great disadvantage that it was not possible to reproduce intricate detail by this method. The sheets were brought into an ornamental form by stamping, punching, hammering and other mechanical processes, the copper foundation often becoming exposed in the process(342).

Jacobi, Jordan and Spencer in their work on electrotyping had been able to obtain thick deposits of firm, coherent metal by the voltaic method but at that moment of time the Elkingtons in Birmingham had obtained only thin deposits of gold and silver which had uncertain adhesion. Many solutions had been tried but without a satisfactory result.

Living close to the Elkington's, but without their knowledge, was a surgeon, John Wright, who in his spare time had made a discovery that was to have a pronounced effect upon the fortunes of the Elkingtons. The direction of the path of his investigations had been very close to that of the Elkington's but with the same very limited results.

One day after a particularly unrewarding series of investigations it is recorded(343) by Percy that Wright told him that he met with a passage in Scheele's Chemical Essays which was to prove of the highest degree of importance to the commercial science of the art, by enabling metallic deposits of silver and gold to be obtained. Speaking of the solubility of the oxides of gold, silver and copper, Scheele states:-(343)

"if, after these calces (i.e. the cyanides of gold and silver) have been precipitated, a sufficient quantity of the precipitating liquor

be added in order to re-dissolve them, the solution remains clear in the open air, and in this state the carbonic acid does not precipitate the metallic calx".

This statement suggested to Wright the probable suitability of the cyanides of gold and silver, dissolved in solutions of the alkaline cyanides, for the purpose of electroplating. He immediately took a solution, composed of silver chloride, dissolved in aqueous potassium ferrocyanide and obtained a thick deposit of firm and white silver by electrolytic action on a vase. The potassium ferrocyanide was used because it was the only cyanide solution available at that moment. A great benefit of the cyanide solution is that the cation concentration is low and there is a copious quantity of the $Ag(CN)'_2$ complex.

i.e. $Ag(CN)'_2 \rightleftharpoons Ag^+ 2CN'$

A low cation concentration is requisite for thick and firm deposits.

It is recorded that Wright[83] then went to London to lodge his patent for this process and in the hotel he met G. Elkington who was also about to go to the patent office. One patent agent was acting for both, and consequently they met.

At this time, 1840, George Elkington was a man of some substance having gained considerable wealth over the years from activities in gilding. Dr. Wright was about thirty years old and at the invitation of Elkington joined in a series of further investigations at the Elkington plant in Birmingham[83].

This discovery turned out to be the major breakthrough in the electroplating of silver and gold.

Unfortunately for his fame, Wright did not obtain protection for his discovery in his own name, the patent having been taken out by Messrs. Elkington in March 1840.[344] The inventor did not live long to enjoy the fruits of his labours, his death taking place in 1844, but the firm entered into an arrangement with his widow to pay her a handsome annuity. She

re-married and lived to a great age and so consequently the Elkingtons did not gain by his early decease. Patent rights were taken out in many countries. Fig. 105 illustrates the Title page of the Belgium patent.

Legal protection having been secured, the patentees were confronted with the greater problem of how to press home their advantage by successful manipulation in the workshop, and by a remunerative output of goods of a quality commending themselves to the public.

11.2.7 Electroplating process scientifically defined

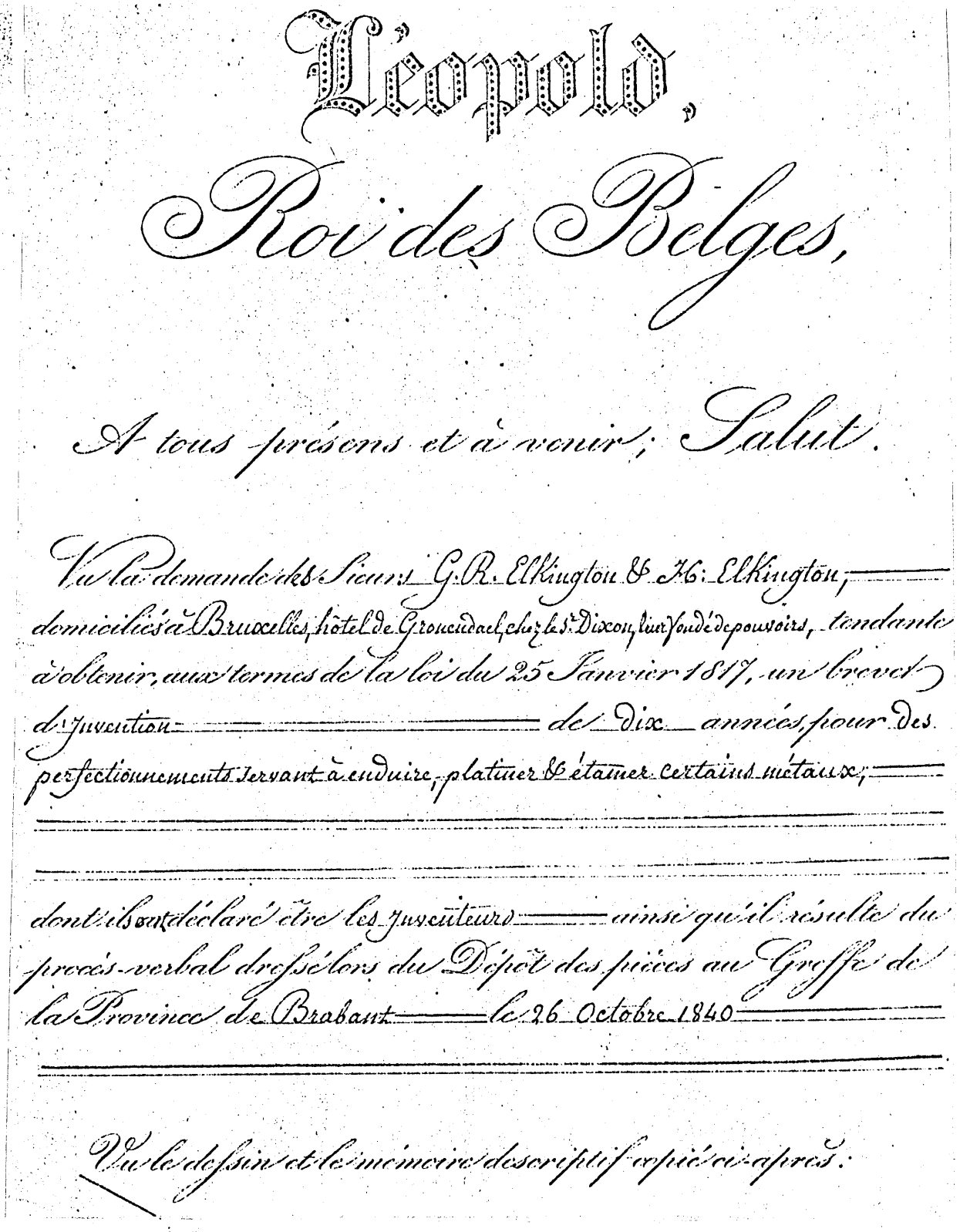
Apart from industrialists who were involved in the process, principally for financial gain, there were others, who having no direct financial interest in the commercial development, could stand back and examine the wider aspects and its implications.

One such person was a doctor of medicine and scientist, A. Smee.

In 1842 he wrote one of the first text books on the electrodeposition of metals and in a later edition he had some interesting comments to make on both the definition of the process and its effect upon the work people.

He stated:(328)

"The term which I have ventured to apply to the science is electro-metallurgy, which comprises, the principles regulating all the arts of working in metals by the galvanic force ..... since my last edition, (in 1842). Electricity is employed not only from the Voltaic battery, but also from the magneto-electric machine. Now, when this work was first written many of my scientific friends thought that the title would have been better had it been termed Voltaic-Metallurgy; and, in fact, the processes were described abroad as galvano-plastics. I dissented from this nomenclature, because it appeared to me that although at that time we could only carry on the process by Voltaic electricity, yet the time would arrive when electricity from other sources would also be employed. That time has arrived; and the magneto-electric machine is now being extensively applied for electro-metallurgy, and thus my term has been fully justified".



Léopold,

Roi des Belges,

A tous présens et à venir; Salut.

Vu la demande des Sieurs G.R. Elkington & H. Elkington, domiciliés à Bruxelles, hôtel de Grouendael, chez les Srs. Dixon, leur fondé de pouvoirs, tendante à obtenir, aux termes de la loi du 25 Janvier 1817, un brevet d'invention de dix années, pour des perfectionnements servant à enduire, platiner & étamer certains métaux;

dont ils sont déclarés être les inventeurs, ainsi qu'il résulte du procès-verbal dressé lors du Dépôt des pièces au Greffe de la Province de Brabant le 26 Octobre 1840

Vu les dessin et le mémoire descriptif ci-après.

FIG. 105 TITLE PAGE OF THE BELGIUM PATENT 8477/1840 INCORPORATING THE 'WRIGHT SOLUTION'.

11.2.8. Intense industrial competition begins

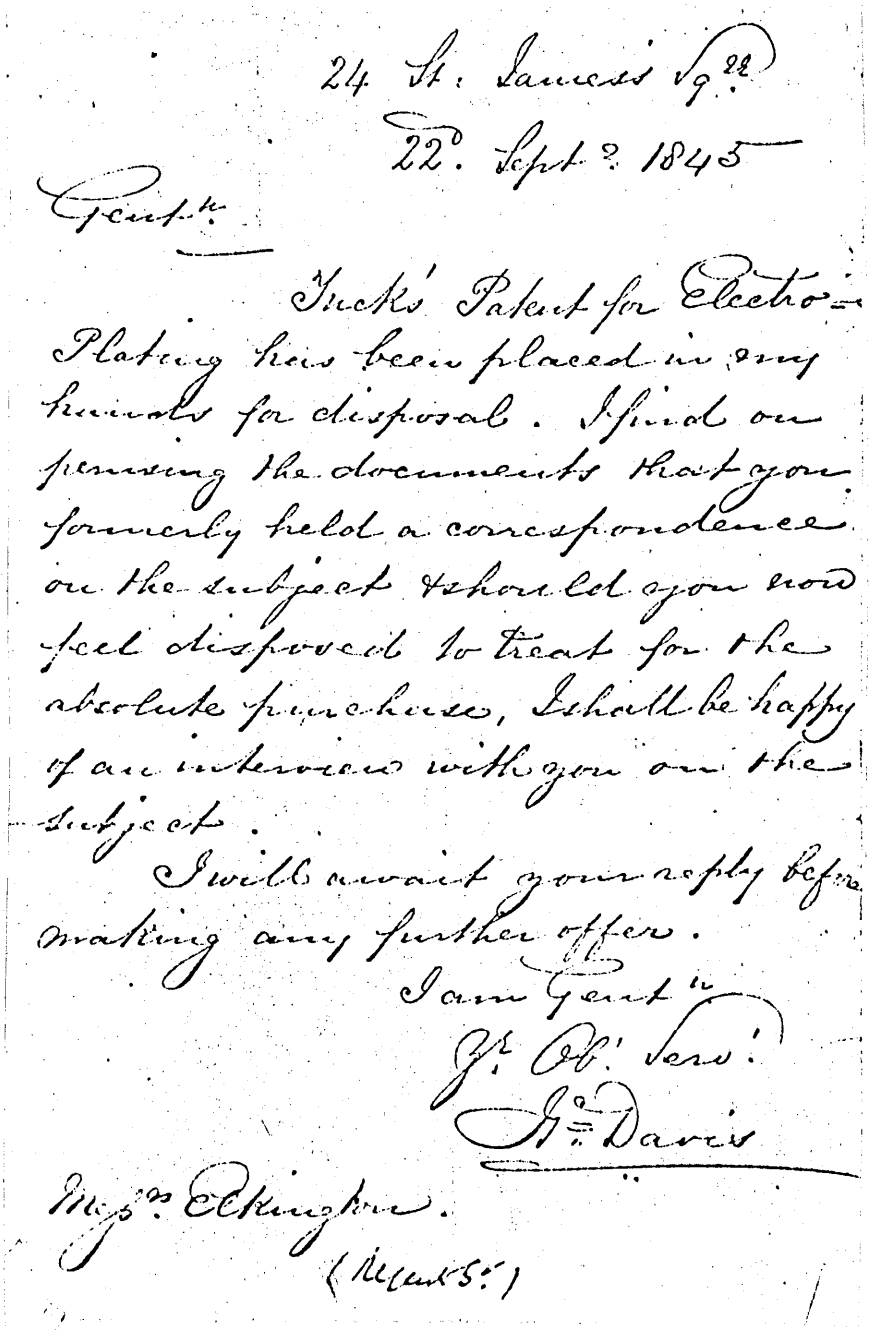
In 1842 Barratt claimed further discoveries, and a long discussion commenced with Elkington, who threatened opposition; eventually the patent was completed[346] and assigned to Elkington. The claims cover a wide field but do not appear to be of much importance; so far as silver is concerned they are limited to the plating of articles by immersion in a boiling solution of sulphide of silver in potash, with or without galvanic current. Barratt obtained yet another patent[347] for depositing by 'an electrical magnetic battery'. The efficiency of electroplating was greatly increased by the researches of H.B. Leeson. He took out a patent on June 1st 1842[90] for improvements, including methods of depositing silver on wax stereotype casts, motions of the articles and agitation of the solutions during deposition, a coating of mercury preparatory to electro-depositions, and claiming some 430[348] salts or other compounds not used before. The motion of the articles and the preparatory processes of "quicking" for obviating the non-adherence or "peeling" of the deposit were of great practical importance. This patent was probably the next major breakthrough after the Elkington patent incorporating Wright's cyanide bath.

Leeson's rights were secured at a most opportune moment, because only three days later on June 4th 1842,[349] Edmund Tuck, a London Silversmith, lodged claims of protection for a method of remedying this defect. Fig. 106 is a copy of Tuck's offer to sell his patent rights to Messrs. Elkington three years later.

11.2.9. Legal disputes in France

A dispute arose at this time between Messrs. Elkington and de Ruolz of Paris. De Ruolz took patents covering the use of solutions for platinum, copper, lead, tin, cobalt, nickel and zinc as well as gold and silver.

De Ruolz had obtained a knowledge of the process from reading Elkingtons' works and had taken out this French patent a short time before the Elkingtons. A long trial resulted.



24 St. James's Sq.re
22. Sept.r 1845

Gent.n

Tuck's Patent for Electro-Plating has been placed in my hands for disposal. I find on perusing the documents that you formerly held a correspondence on the subject & should you now feel disposed to treat for the absolute purchase, I shall be happy of an interview with you on the subject.

I will await your reply before making any further offer.

I am Gent.n
Y.r Ob.t Serv.t
G.o Davis

Mess.rs Elkington.
(Messrs.)

FIG.106 TUCK'S OFFER TO SELL PATENT RIGHTS TO MESSRS. ELKINGTON (ELK. REC.)

The following is the text of a letter sent by the Elkingtons to the French Jury.

"Gentlemen,

When an academic judgement placed M. de Ruolz and myself in the same rank for the invention of new processes of Electro-Chemical Gilding and plating, I contented myself by the claim which was made in my name by my representative M. Truffant. My relations with M. de Ruolz allowed me then to believe in the honour of his character though it appeared to me extraordinary that he had truly made the same discovery as myself, and that several months after the taking of my Patents and their publication in several periodicals.

...Today, having read the latest publications of M de Ruolz and being able to judge how very disloyal is his conduct towards myself and my honourable friend M. Christofle who has so well directed in France the exploitation of the new invention, it becomes my duty to protest against all the assertions which villify our statements, and to claim my rights in their entirety....

Signed

G. Elkington

The trial was very costly and it was reported[350] that the industry was "nearly brought down to its knees." It was established that Messrs. Elkington were the original patentees of the potassium cyanide solution and it was finally settled by a compromise between de Ruolz and the patentees for the use of the process.

11.2.10. Magneto-electric Machines used for electrodeposition

An event of importance to electro-plating occured, at this time namely that the application of the magneto-electric machine to the process. A machine for this purpose was patented by Woolrich of Birmingham in August 1842[92].

The early commercial development of electroplating had followed from the availability of a steady source of current from the Daniell cell. However, the Daniell cell could not provide enough electricity for the industry when large currents were consumed.

The patent describes the invention of:-

"a magneto-electric machine for use in applying current to the coating of metals" Fig. 107 shows the machine.

Percy wrote of the machine:- (416)

"I had the pleasure of conducting Mr and Mrs Michael Faraday around Prime's works and for the first time he saw his discovery of magneto-electric current applied to the deposition of silver. I shall never forget the sparkling delight which he manifested on seeing the result of his purely scientific labours rendered subservient to a beautiful art and to the advantage of others"

An estimate of the saving involved by replacing the constant battery with the 'constant current machine' was made by Bouillet in 1881:- (351)

"In order to illustrate the importance of the industrial revolution accomplished by the Gramme machine, we will give you some figures of absolute correct cost prices, for they are established on a considerable production and on average of five years manufacturing work.

With the battery, the kilogramme of silver entailed an expenditure of 3.87 francs for the galvanic current.

With the Gramme machine, taking into account the value of the motive power, the interest of the capital, and the wear and tear of the material, the cost of depositing silver is reduced to 94 centimes per kilogramme (0.94 franc)."

11.2.11. Elkington purchases Woolrich patent

There was another novelty in the Woolrich patent which consisted in the application of the "double sulphites" of silver, gold and copper, with the alkalies as depositing solutions." Woolrich's specification contained full instruction for preparing the various salts for depositing silver, gold and copper. (patent 1842/9431)

Only a few years previously the patent of Elkington had been taken out, and in order to protect his interests from the possible threat of this new process, Elkington decided to purchase the Woolrich patent. Fig. 108 is a copy of the letter in which Woolrich offers to sell his patent for £15,000.

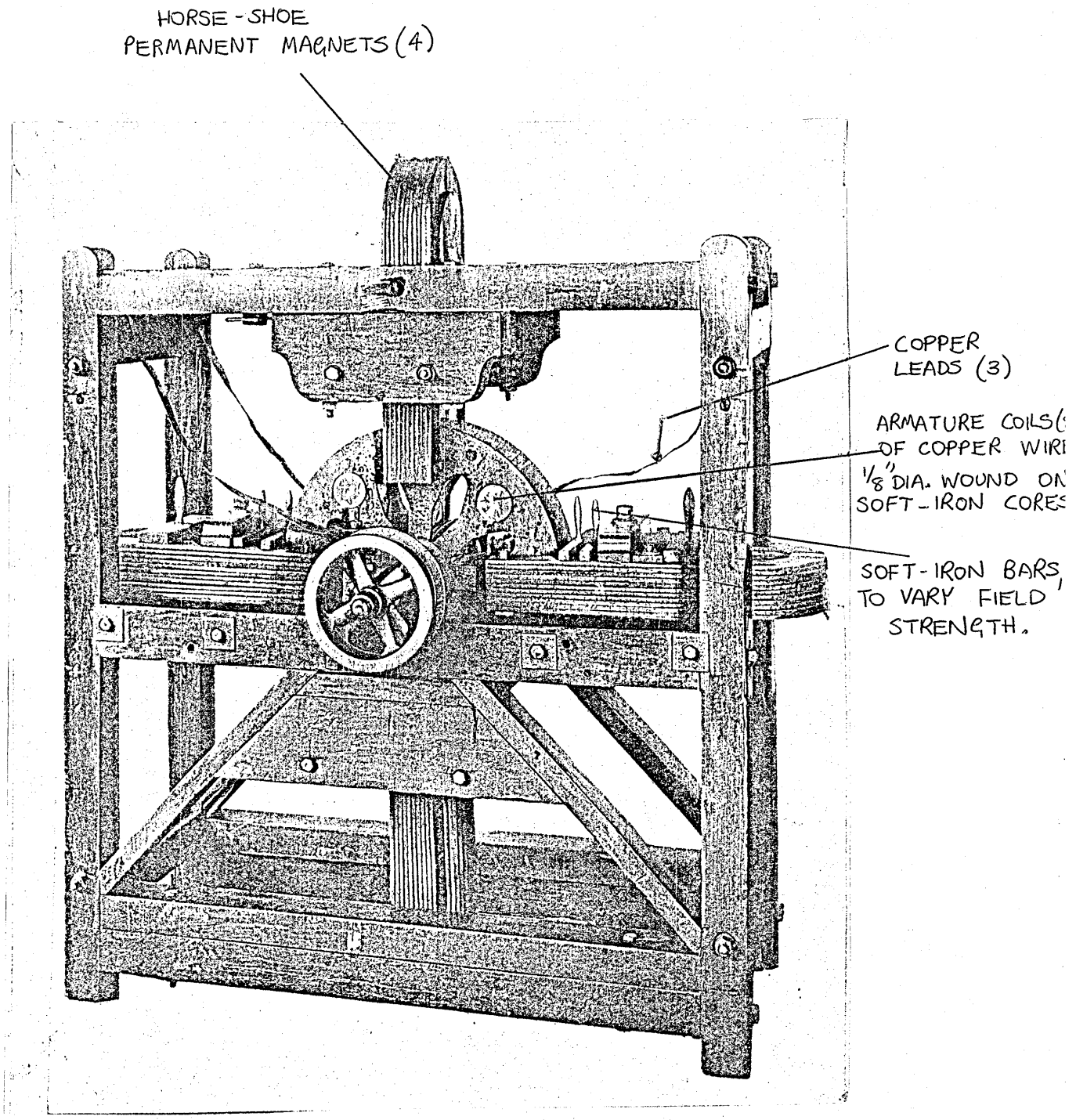


FIG. 107 THE WOOLRICH MAGNETO-ELECTRIC PLATING MACHINE (1844) (352)

6 Cadogan Buildings
April 1st 1843

To Messrs G.H. & H. Elkington
Newhall St. Birmingham

Gent-

Having now completed the arrangements for continuing with Mutter the purpose of Articles formed of Metals or Metallic alloys" — I offer to sell you the Patent for the same for the sum of Fifteen Thousand pounds and I give you until Tuesday next to decline or accept my offer

Yours very respt

John Stephen Woolrich

FIG. 108 COPY OF LETTER FROM J.S. WOOLRICH IN WHICH HE OFFERS TO SELL THE PATENT 1842/9431 TO G.H. & H. ELKINGTON (ELK. REC.)

11.2.12 Millward introduces carbon-di-sulphide to ensure brightening

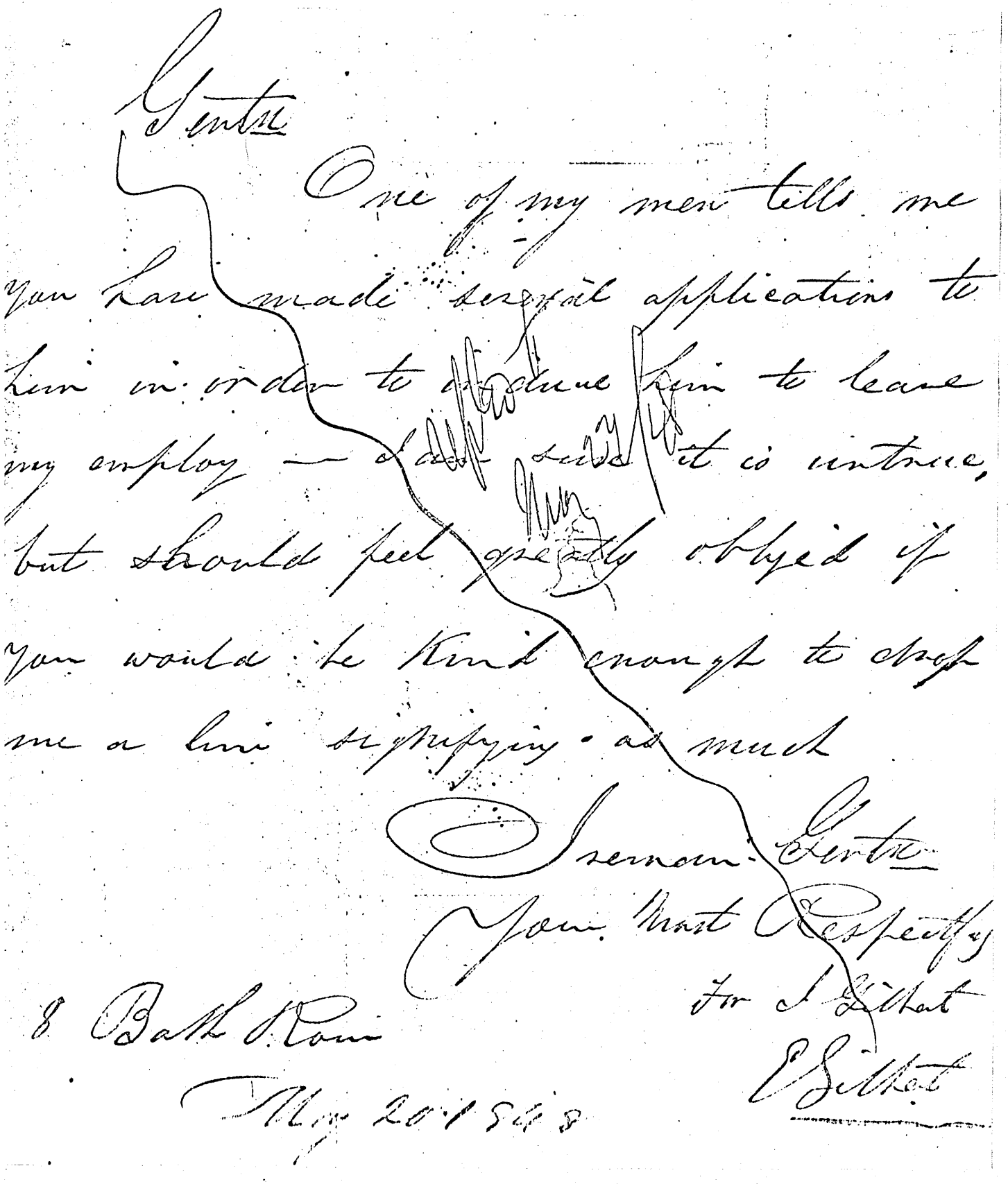
The surface of silver deposited from the ordinary cyanide of silver and potassium plating solution was found to have a frosted appearance and it was found necessary to burnish this by mechanical means. This with articles of highly figured design, was a great disadvantage, as the process of burnishing was tedious. This problem was overcome by Millward who was employed at Elkingtons. The circumstances leading up to his discovery are as follows:-(91) In the process of copying figures for electro-typing by a mixture of wax and resin, the surface of the wax is covered with a film of phosporous by means of a solution of phosphorus in carbon disulphide. It was observed by Millward, that when these prepared wax moulds were put into the cyanide plating solution for the purpose of silver plating, other articles such as spoons, forks etc. which were being plated in the same vat and especially those nearest to the wax moulds, acquired a coating of near perfect bright silver, which occurred sometimes in patches, and sometimes extended over the articles. This circumstance attracted attention, and induced Millward to try the effect of adding carbon disulphide alone to the plating liquid. Considerable success soon resulted, but at this juncture the secret escaped, and in consequence a patent(353) was taken out in 1847, by Millward and a Mr. Lyons, who had acquired a knowledge of the secret. Morris Lyons was also an operator at Elkingtons and with Millwards brothers, Richard and Arthur had carried this knowledge to another firm of Birmingham platers.

11.2.13 Range of electroplated metals extended

11.2.13.1 Platinum

M. Roseleur was the first to succeed in obtaining good platinum deposits(328) in 1847. The following is the process which he indicated as suitable for depositing on copper or its alloys:-

Ten grammes of finely laminated platinum were mixed with 150 grammes of hydrochloric acid and 100 grammes of nitric acid at 40° centigrade. The solution was then heated until it became viscous and after allowing it to cool and dissolving it in 500 grammes of distilled water, it was filtered.



Sir

One of my men tells me you have made several application to him in order to obtain him to leave my employ — I do not wish to interfere, but should feel greatly obliged if you would be kind enough to stop me a few shillings as much

I remain Sir
Your Most Respectfully
For J Elliot
J Elliot

8 Bath Row
May 20th 58

FIG. 109 ELKINGTONS ACCUSED OF SEDUCING WORKMEN (ELK. REC.)

At the same time 100 grammes of ammonium phosphate were dissolved in a similar quantity of dissolved water, and the two solutions were mixed. After further preparation the solution was then ready for deposition on copper.

'Platinating' metals by the use of galvanic currents was described by Smee in 1851 as a new process.

The process at this time was considered to be more difficult than gilding.(328)

The object was first thoroughly cleaned with potash and a solution of platinum prepared. A fine platinum wire was connected with the silver of a compound battery and the article to be plated connected with the zinc of the battery and then placed in the solution('nitro-muriate of platinum').

11.2.13.2 Cadmium

The earliest recorded attempt to deposit cadmium was made by Russell and Woolrich in 1840(354) but the practical deposition only became a reality in 1920.

According to Smee(325) great difficulty was found in obtaining firm and coherent deposits from solutions of either its chloride or sulphate; but some success was obtained in depositing Cadmium from a solution of the ammonium sulphate, prepared by adding sufficient aqueous ammonia to a solution of cadmium sulphate.

Napier(354) recommended the following method:-

"A solution of cadmium is easily prepared by dissolving the metal in weak nitric acid, and precipitating it with carbonate of soda, then washing the precipitate and dissolving it in potassic cyanide. This solution must be heated to 40°C and electrolysed by a current of 4 to 6 volts. The deposited metal is white, and resembles tin. It is very soft and does not offer any important advantage in industry".

It is probable that the process would have been perfected well before the 1920's but the key to this delay can be found in this last sentence quoted from Napier. This illustrates fully the dependence of industrial development of a process upon the commercial necessity.

The electro-plating industry entered into the second half of the nineteenth century with a maintained momentum.

Interest in the process was continuing on the Continent. An interesting short article[355] by M. Bouillet in 1852 on "Facts relating to the history of galvanic plating" attempted to press the claim of Elkingtons as distinct from those of de Ruolz, for the discovery of practical electroplating. Bouillet was the Chief Chemist for the Christofle electro-plating company in Paris which had a licence from the Elkingtons for electro-plating a number of metals and so he would naturally have had a vested interest.

Thomas and Dellisée[356] also in 1852 and Bolley[357] the following year each gave a paper on the practical aspects of depositing silver. This was followed in 1856 by a further article[359] on "Practical rules in Electro-deposition" by Gore, indicating that the industry was definitely at the stage of practical electrodeposition.

11.2.13.3 Tin

Up to 1850, the electro-platers' practical interest had centred mainly around gold, silver and copper, but gradually this was extended to other metals. Electro-tinning was considered to be very difficult.

Smee stated:[359]

"To obtain a thick layer of tin directly by electricity, would be extremely difficult, and although a thick layer may be readily obtained by depositing either crystalline or spongy tin, and then fusing it, I cannot see that any advantage is likely to accrue from such a proceeding. Perhaps the sulphate of tin is the best solution that can be used for this purpose, conjoined with the single battery process".

However the first practical process was developed by Roseleur[360] in 1850. He stated :-

"The bath was composed of 50 litres of distilled water, 500 grammes of pyrophosphate of sodium and 50 grammes of melted stannous protochloride. The water was contained in a vat entirely lined with sheet tin or tin anodes, the pyrophosphate was poured in and the mixture stirred until it was dissolved. Stannous protochloride was then introduced, and the solution again stirred until it was in complete dissolution. The liquid then became clear and almost colourless." (360)

Tin is used as a coating material because of its high corrosion resistance in many media and consequently a large proportion of tin goes on the manufacture of tin-plate.

It is resistant to solutions of non-oxidising salts, but corrodes rapidly in solutions of salts of metals more noble than itself.

Tin has a more negative potential than iron when in contact with the majority of conserved products, but in some types of tinned products, the potentials are reversed and local perforation of the wall can occur.

11.2.13.4 Lead

One of the first scientists to deposit lead was de Ruel z in 1840 (359) but the process only became practicable at the beginning of the twentieth century.

M. Roseleur, however, was able to produce coloured rings on polished steel plates by means of preparations of lead salts in the mid nineteenth century. He stated:- (360)

"The object to be coloured, attached to the negative pole, is immersed in a cooled bath of plumbate of soda; a platinum anode is then gradually dipped into the liquor without touching the object with it. The latter is immediately observed to become coloured with a variety of lines yellow at first, and each of these colours grow darker and completely change as the platinum anode is more or less deeply immersed. These lighting effects which are caused by the greater or lesser thicknesses of the deposited plumbic acid, can be indefinitely varied".

A similar variation to this was produced by Watt, but he used plumbous acetate instead of the protoxide. (SEE 360)

When a sheet of copper cut in a star shape was attached to the anode, the colourations on the plate were effected in an analogous way. If a piece of cardboard was placed between the conducting wire and the plate, the colourations took place outside this screen.

The colours so produced resembled those of a prism, but they did not adhere firmly to the metal and consequently had to be coated with a layer of varnish before they would adhere. However for all practical purposes no success was obtained at this time on the electro-deposition of lead and Smee stated:-(359)

"Electro-leading is a process equally unfavourable as electro-tinning, in its result. The tri-nitrate of lead* makes perhaps as good a solution as can be employed for this purpose".

Towards the end of the nineteenth century the French obtained lead deposits satisfactorily however from dissolving 10 grammes of litharge (protoxide of lead) in 100 grammes of caustic potash(359). This was all mixed in 2 litres of distilled water with some litharge added occasionally. A lead anode was used.

The American depositors(361) simply dissolved plumbous acetate or nitrate in water. The lead was found to be easily deposited when the solution was only slightly concentrated and the current weak. For laboratory experiments an alkaline bath was used. It was prepared by precipitating the "lead of plumbic acetate or nitrate by potash," soda or ammonia(361) and dissolving the precipitate in potassic cyanide.

The first person to have any practical success with the electro-deposition of lead was Betts in 1901, but the process was not perfected until Mather's contribution in 1910.

Lead had been used since ancient times as a metal which is resistant to water, to the atmosphere and a large number of aggressive solutions. Under some conditions, the corrosion resistance of lead is very high.

Distilled and soft water however attack lead, and water containing large quantities of carbon dioxide is particularly detrimental. It is

* term not clear.

however resistant to corrosion in soils and is consequently used as a material for the manufacture of cable sheathing, but relatively little as a conventional coat. (SEE 7.4)

11.2.13.5. Palladium

To palladiate articles, Smee used similar methods to those he used in platinating them.

Smee stated:-(359)

"We employ ammonium muriate of palladium dissolved in liquid ammonia*, and employ the compound battery, process with a small positive platinum pole. The palladic-cyanide of potassium with a palladium pole may also be employed. This metal is whiter than platinum, but not so bright as silver".

It was found that palladium adhered with such firmness to copper, when reduced by voltaic electricity, so that it was almost impossible to remove it when once deposited.

11.2.14 Elkingtons approached by Krupp of Essen

In 1851 the Elkingtons were approached by Alfred Krupp of Germany, who was interested in the developments that had taken place in electroplating, for applying the technique to spoons and forks in large quantities. The trouble was the slow and costly manipulation required to shape the raw material of the article preparatory to plating. It was with machinery for rolling and cutting the metal and stamping out blanks that Alfred Krupp found his way to Birmingham. He undertook not only to supply machines and to license their use, but also to install them. He supervised the erection of new mills for the Elkingtons in Brearly Street, Birmingham. The result of this activity was that he returned to Essen with £8,000. Fig. 110 shows a copy of a letter from Krupp stating that he was going to visit Birmingham with an operator.

* possibly $(NH_4)_2 PdCl_4$ From $PdCl_2 \xrightarrow{HCl} H_2PdCl_4 \xrightarrow{NH_3} (NH_4)_2 PdCl_4$ dissolved in aqueous NH_4OH

11.3 Dynamo supplements, then supersedes primary cell (Circa 1836-1900)

11.3.1 Crystal Palace Exhibition

In 1851 an event of considerable importance took place which provided a great deal of publicity for the electroplating industry. This was the Crystal Palace Exhibition. On display were a great variety of articles and the public at large became aware of the practical benefits of the process. Consequently a demand began to be created for electroplated goods.

In 1852 in the Illustrated Exhibitioner there is an interesting article on the Elkington Works:-(95)

"..... The patentees employ upward of five hundred work-people. In addition to their immense production of electroplated goods, the process is extensively adopted in France and in other foreign countries and there are thirty other manufacturers in England licenced to use the process".

"..... What has been accomplished is strikingly apparent on an inspection of their showrooms, which, astounding as it may seem, are longer than the body of the far-famed Birmingham Town-Hall, though, of course, they are not to be compared in height with that splendid pile.

"Glass-cases stand on either side, while in the middle are three others in which magnificent centre pieces and candelabra are displayed (Fig. 111)." The article continues to describe the various processes, many of which are outside the scope of this work, but then goes on to supply details of the plating process.

Messrs. Elkington Mason & Co.

Birmingham

Gussstahlfabrik bei Essen in Rhein Preussen 6. March 1851.

Gentlemen!

According to your remarks the alterations of the rollers respecting the thread and the flutter surface of handles are since executed. The two sets of fiddle and thread pattern are complete and shall be forwarded to You without delay. At their arrival the manufacture may be put into full activity.

The writer of the present will then come to Birmingham and bring You the same man, who did set at work former supplies of the same kind and leave him till his information to your men will make him superfluous. Kings and Lily pattern shall be completed during the first fortnight of activity and we shall commence with one or two pair of either. I am only waiting for Your account that all is ready and wish to see that day as near as possible. Excuse this late answer considering absence of the writer. Respectfully

Yours respectfully

Fred. Krupp

FIG. 110 LETTER FROM F. KRUPP STATING THAT HE WOULD BE VISITING BIRMINGHAM WITH AN OPERATOR. (ELK. REC.)

In fig. 112 the Woolrich Magneto-electric Machine is shown on the left and the vats on the right. "Metal rods were placed across the vats and to these articles immersed in the solution were attached by thin wires, and between the vats passed a metal tube to convey the electric current to the rods. Since an immense consumption of silver is thus going on, plates of pure silver were placed in the vats connected with another metal rod, conveying a negative current of electricity, which constantly discharged silver into the solution. The process of electroplating in gold was precisely the same as that in silver. The aggregation of silver was continued until the desired thickness is obtained; and in this way articles might even be made solid."(95)

11.3.2 Development of Woolrich Magneto-electric Machines

It is difficult to determine just how many magneto-electric machines were built between 1842 and the 1850's but there is one machine with a date of 1851 marked on it, made to the basic Woolrich design, which is now at W. Canning Company, Birmingham, as an historic reminder of the industry's past. (Fig. 114)

In general appearance it is a great improvement upon its predecessor. It has a cast-iron frame in two pieces, about 4 feet high, the front and back sections being bolted together, The machine, to the top of the upper magnet is almost 5 feet high, and the total weight is nearly a ton. It is a 4-pole machine, each of the permanent magnets being 30 inches long and $9\frac{1}{2}$ inches wide and formed of 10 laminae of $2\frac{1}{2}$ inches by $\frac{3}{8}$ inch hardened steel. The discs are distinct from the 1844 machine, in not being ventilated on the side.

Owing to the absence of adequate provision against overheating, neither of these two machines could have been operated at anything like the full output of which they would otherwise have been capable.

It is natural to consider what part, if any, the firm of Elkingtons played at this time in the application of the magneto-electric machine to electroplating.

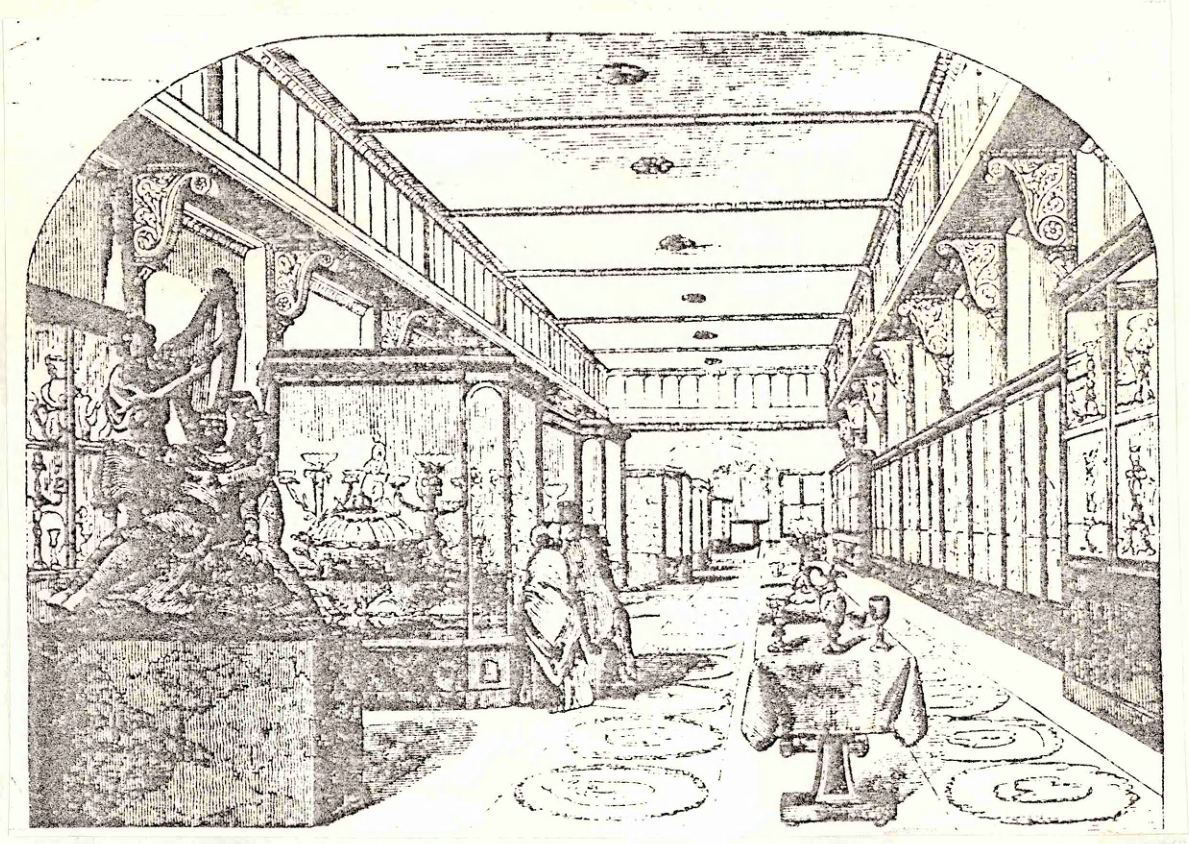


FIG. 111 THE SHOW ROOM AT MESSRS ELKINGTON BIRMINGHAM IN 1852. (95)

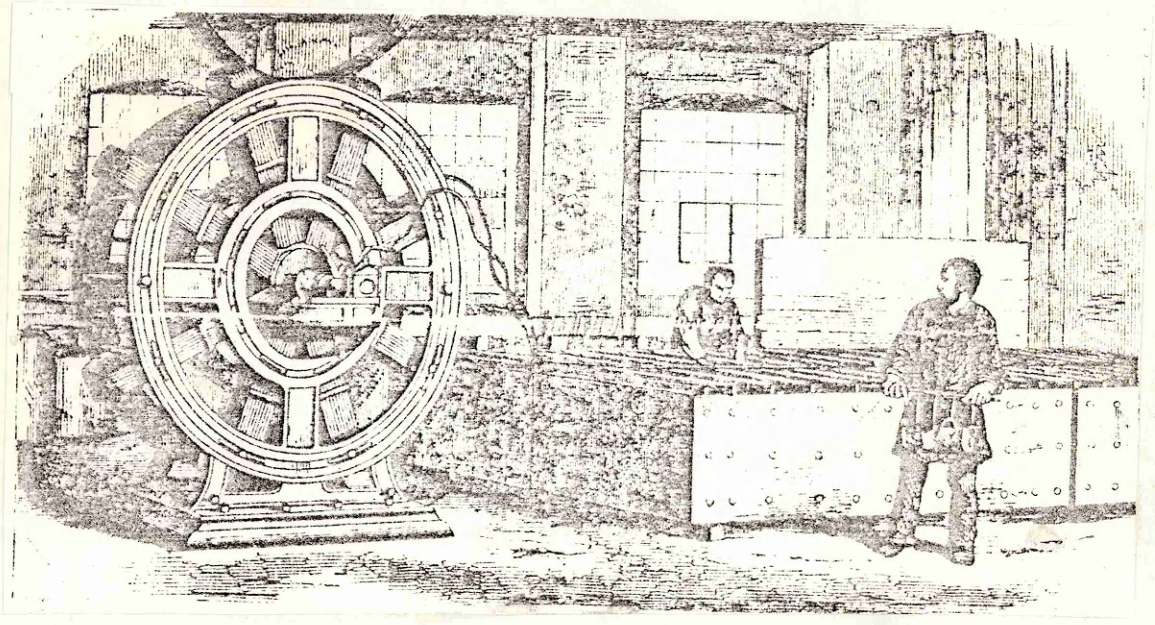


FIG. 112 THE ELECTROPLATING ROOM

A WOOLRICH MAGNETO-ELECTRIC MACHINE

IS SHOWN ON THE LEFT SIDE (95)

GREATER DETAIL OF THE VAT IS SHOWN

IN FIG. 122.

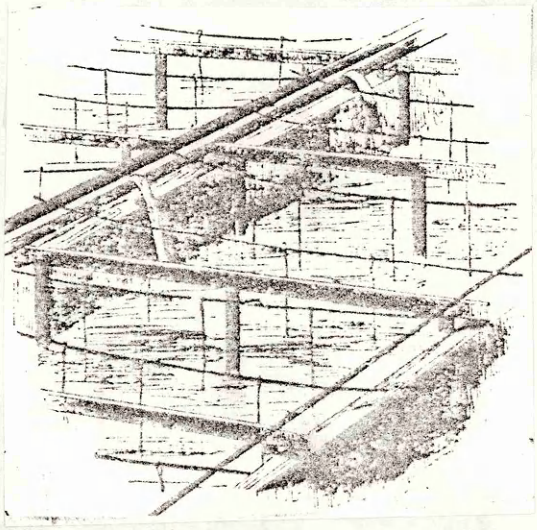


FIG. 113 DETAILS OF THE ELECTROPLATING VATS (95)

As late as 1850 Mr Elkington considered[362] that he had never been induced to give up the primary battery "in favour of magnetism".

However he must have changed his ideas very quickly after this, for in 1852[363] (fig. 114) there appears to be an eight-pole magneto-electric machine standing about seven or eight feet high.

It stated:-"The armature of the machine, set in motion by a small steam-engine revolves six hundred times in a minute. At a short distance from the poles is a series of sixty-four permanent magnets arranged in a circle. One great advantage secured by the machine is the regularity of its action. An ordinary battery decreases in power most materially in a few days; while this machine has been in operation almost continually day and night for six months, with scarcely any perceptible variation in its energy. It will deposit fifty ounces of silver per hour".

In another part of the article it states:-"..... up to a recent period, galvanic troughs were the only means employed for producing electricity".

From these three indications, it can be deduced that Elkington's probably introduced the application of the magneto-electric machine into electroplating in 1851.

11.3.3 Early electrodeposition of zinc in Britain

Considerable interest had been shown in France from 1840 in the electrodeposition of zinc but the earliest patent for electrodepositing zinc in England was taken out by C.P. Person,[364][365] on April 27, 1854 and reads as follows:-

Coating with Zinc by Galvanization:-

"The zincing is effected by electrodeposition from a bath containing salts of zinc and alumina. The solution may be prepared by dissolving precipitated alumina in a solution of sulphate of zinc. The zinc may be deposited from such a solution on all metals viz: iron copper etc. and the adhesion is complete if care is taken previously to make the surface of the article bright".

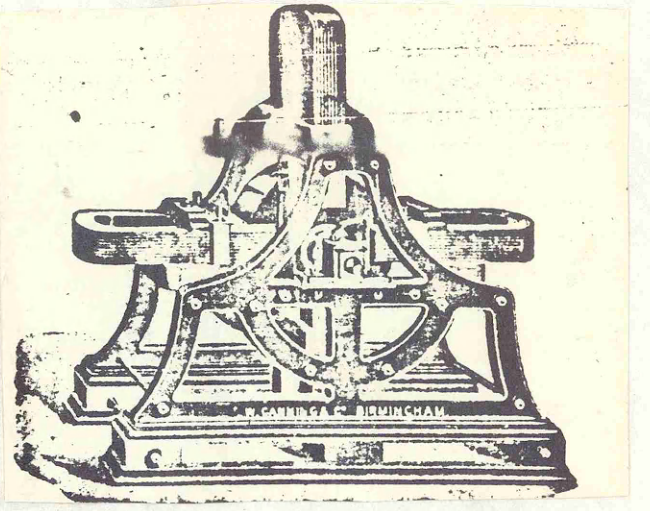


FIG. 114 A MAGNETO-ELECTRIC MACHINE CONSTRUCTED IN 1851 ON THE BASIS OF WOOLRICH'S EARLIER MODEL. (95)

However no significant progress in the electro-depositing of zinc on a practical scale was to take place for a further 40 years.

An article[366] by Gore on the "Inductive view of Electro-Metallic Deposition" of metals was published in 1853. Also two patents by W. Millward[367] (one of Elkingtons platers) and S. Hjorth[368] both on "Electro Magnetic Apparatus" were also recorded, but the significant development from this time was that of the practical electrodeposition of nickel.

11.3.4 Practical Electrodeposition of Nickel initiated in America

In 1842 Bottger[328] had patented nickel-ammonium-sulphate baths, but it was not until 1858 that Adams in Boston, America, carried out the first commercial electroplating.

Adams recalls:-[94]

I had been investigating the electrolytic possibilities of many nickel and cobalt salts, so that I had become familiar with the properties of these metals, both in the pure fused condition and in the form of electrotypes. These latter were small sheets of from three thousandths to five thousandths of an inch in thickness, stripped from polished sheets of brass used as cathodes, of about 3 by 4 inches in dimension. Precisely how the thing came about I cannot at this distance of time recollect. It will suffice to say however, that I somehow managed to interest Mr. Joseph Smith, of Boston, a dealer in gas fixtures, to start the business of nickel plating cast iron gas taps, he to furnish the capital and I to do the plating. So it happened that in the winter of 1865-6, I commenced operations with cast nickel anodes. I may say, that I took out a patent at the time[369] for a nickel plated gas tap as a new article of manufacture".

Adams' patent was based on Bottgers,[328] original nickel-ammonium-sulphate bath with the modification that solutions and anodes of high purity were specified (particular emphasis being placed on the absence of nitrates), and the bath was operated at low current density to avoid passivity of the anodes.

The next attempt at nickel plating was carried out by William Remington. He specialised in such articles as teaspoons and harness

hardware, and these as far as outward appearance was concerned were of good quality(94).

Mr. Remington's plating shop was also located in Boston and contained several plating tanks holding, in the aggregate, from 400 to 500 gallons of nickel solution, a hot caustic soda bath and a hot copper cyanide bath. The electrolyte used was originally a solution of nickel chloride, with an excess of ammonium chloride. He employed between 15 and 20 employees.

Adams had cause to visit Remingtons plating shop on one occasion and observed:-

"Mr Remington used a current of very high voltage, and had to, for lacking that, no nickel was deposited, and if any attempt was made to thicken the deposit, the metal rippled up into minute brownish spangles, a totally useless covering. Twenty-four Grove's cells in series I found in one tank. Mr. Remington's efforts ended in utter failure. In order to render his solutions more efficient he used numerous 'dopes' mostly of vegetable origin. The last 'dope' tried was an aqueous infusion of skunk cabbage.(94)"

By 1869 the commercial use of nickel plating was becoming firmly established in America with larger premises being opened in Boston and also in New York. At this time little was known about the chemical, electro-chemical or even the mechanical properties by the majority of platers.

In general there was not a great deal of difficulty with the nickel solutions. The trouble was that the same methods were used in preparing nickel that were used in depositing silver.(94) Deposited nickel is very hard, whereas silver is a very soft metal.

Deposited silver could be burnished and a lustrous finish obtained, but a nickel deposit was found to be too hard and consequently had to be polished.

The process at this time consisted of first buffing followed by dipping in a hot or boiling solution of caustic potash, in order to saponify whatever grease remained on the surface. After withdrawal from the hot potash solution, it was rubbed with a pumice stone which unfortunately badly scratched the material if it was brass. The article was then washed in water

and placed either directly into the bath or immersed in a solution for oxide removal. Due to the preliminary process, the articles had a relatively rough surface and the platers were consequently compelled to put on a sufficient coat to cover up all the scratches. This resulted in extra nickel being required and a loss in time.

The next major development came from Edward Weston. He stated:-(370)

"It occurred to me that we ought to be able to get softer nickel, but at first the only way I could do it was by reducing the rate of deposition; keeping down the tendency of the evolution of hydrogen at the cathode. Some years ago I was rewarded by finding a solution which yielded a nickel deposit with characteristics closely approaching those of good copper. It could be rolled and drawn and I called it 'malleable nickel'. I think that was the first time malleable nickel had been produced by the electrolytic cathode. The anode was made from 'grain nickel' mixed with a small amount of carbon with a binder of tar or pitch. The compound was then submitted to hydraulic pressure. The solution used was sulphate of nickel, or chloride of nickel to which boric acid had been added. I could have added any other acid and prevented the precipitation of the salt of nickel at the cathode but I had sound reasons for not doing. If I added another acid which had a tendency to attack the positive metal to be coated, I would have secondary reactions set up immediately upon my putting the electropositive metal into the bath, and it turned out that boric acid was the most suitable. The patent was unfortunately drawn so that afterwards others put in acetic acid. You can put in other acids - just keep the solution slightly acid and 'it will go'." (370)

11.3.5 Practical electrodeposition of Nickel spreads to Europe

In 1869 Weston and Quintart visited England, France and Germany, with a view of establishing the nickel plating industry in Europe. A small experimental shop was established in Liverpool and within a year a fully equipped plating establishment of about 600 gallons' capacity was operational in Birmingham.

A shop under the management of a Mr. A. Gaiffe, a well-known manufacturer of scientific instruments in Paris, was opened. It had a capacity similar to the one in Birmingham(57).

In England, the Elkingtons in Birmingham appeared to be a considerable help where they thought the 'new plating' could be usefully applied.

The art was carried on substantially as it was in 1869-70 with the same solutions and with the same anodes well into the twentieth century. It was, therefore, only when methods had been devised for maintaining a low acidity of the nickel bath that it became possible to establish nickel plating on an industrial scale. Adams' had achieved this by utilising the bath recommended by Bottger as early as 1843, eliminating deleterious impurities, such as nitrates, and maintaining a low current density at the anodes to avoid passivity which had previously been a major factor in causing the solution to become excessively acid and yield unsatisfactory results.

Nickel plating became so popular because of the properties of the electrodeposit of being protective and decorative.

The potential of nickel is more electro-positive than that of iron and so nickel coatings can only protect steel mechanically against corrosion. They do not give electrochemical protection. Steel can be protected against corrosion only by a relatively thick nickel coating and therefore nickel plating with an undercoat of copper gradually began to be used in practice. Sometimes a combination of coatings was used:- first coating-nickel, intermediate layer - copper, and final layer - nickel.

The real impetus in establishing nickel plating on a sound and permanent scale in France came in 1871. This was due to the introduction of the 'constant current' machine.

M. Henri Bouilhet, an eminent chemist of the firm of Messrs. Christofle in Paris, at a conference in 1881 recalled:-(351)

"Nickel plating has gained favour during the past few years not because of better or new solutions, but because the electric industry has become enriched with a source of electricity better, more constant, and

FIG. 116 AN ENGRAVING OF LOUIS XIV's ELDEST CHILD, STRUCK IN FRANCE FROM THE FIRST NICKEL ELECTROTYPE EVER MADE.

infinitely cheaper than the batteries. We mean the Gramme machines which have caused a real industrial revolution, and which have rendered inestimable services to electro-chemical depositing manufacturers".

11.3.7 Electrodeposition of chromium

During the nineteenth century methods of producing deposits of chromium from a chromic acid solution were suggested by Bunsen in 1854,(328) but there was no sign of any recognition of the industrial potentialities of this metal as a decorative, untarnishable coating.

As late as 1910 Cooper states:(371)

"Chromium is a very hard infusible metal, which so far has not received commercial application".

Attempts to deposit chromium from a solution of chromium sulphate with small additions of boric acid using a lead anode and a copper cathode resulted in smooth deposits being obtained, but great difficulty was found in getting a thick deposit owing to the formation of cracks.

11.3.8 Electrodeposition of zinc

During the last decade of the nineteenth century, the major interest was centred around the electrodeposition of zinc primarily because of its universal acceptance as a protective metal. The earliest patent for electro-galvanizing in England had been taken out by Person in 1854.(364)(365) From this period there was a lull in the further development and commercial use of the process. Manufacturers became suspicious since, although in theory electro-galvanizing was simple, in practice it was found to be very unreliable. The popularity of hot dip galvanizing had rapidly gained momentum and the electrogalvanizing process began to become neglected.

An article in The Engineer stated in 1895:(375)

"Zinc applied to iron and steel articles by placing them in an aqueous solution of zinc sulphate, chloride, or any other well known electrolyte, does not afford such a good protection to iron and steel as an equal thickness of zinc applied by the hot or molten process; and great difficulties are experienced with ordinary zincing solutions by the appearance on removal from the bath, of dark, unsightly patches on the work, mainly due to the occlusion of hydrogen".

As distinct from the hot galvanizing, the electrogalvanizing process required considerable skill, because of all the varying influences that could effect the result of the final product.

One of the problems was that an insoluble scale formed on the surface of the anode and consequently there was an increase in the electrical resistance.

The scale was also a source of constant trouble since detached pieces had a tendency to settle on the work and render the zinc plating defective. Attempts had been made to overcome a problem of the insolubility of zinc anodes by placing granulated zinc in the bath, but in practice such an arrangement was found to render little or no assistance.

The fortunes of the process rose when in 1895 Sherard Cowper-Coles took an interest in it. Many of the problem areas he investigated, he made improvements in the techniques and so removed some of the uncertainties.

The electrolyte in a bath must not be allowed to stagnate in order to prevent uneven coatings and one way to prevent this was developed by Cowper-Coles. He developed a method of regenerating the electrolyte by pumping it through a filter of coke and zinc dust. Another method used to maintain a 'fresh' solution was to place the anodes at the bottom of the vats whenever possible, unless anodes and the work could be stacked vertically, so that gas bubbles given off from the surface would percolate through the solution.(375)

Another feature of the improvements Cowper-Coles made was the introduction of insoluble rotatable anodes. These anodes were made in a variety of shapes to suit the components being galvanized. Since the thickness of a deposit varies as the square of the distance from the anode, the size and layout of the anodes had to be designed so that each part of the work was equally distant from them. Different anode layouts that Cowper-Coles introduced are illustrated in Fig. 117a, the method of suspension being shown in Fig. 117b.

Fig. 117c gives a general view of a electrogalvanizing plant erected to Cowper-Coles' specification. Zinc dust was added to the regenerating tanks.

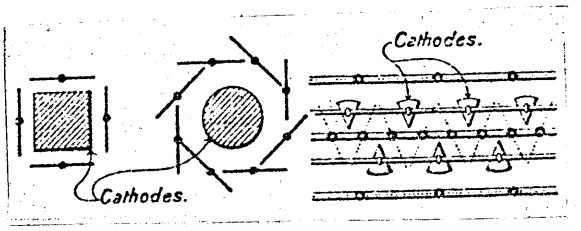


FIG. 117(a) ROTATABLE ANODES

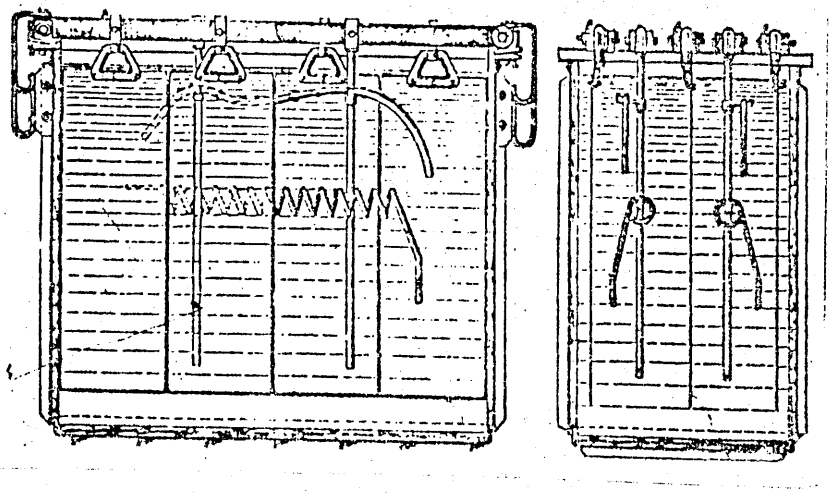


FIG. 117(b) GENERAL ARRANGEMENT OF ELECTRODES (375)

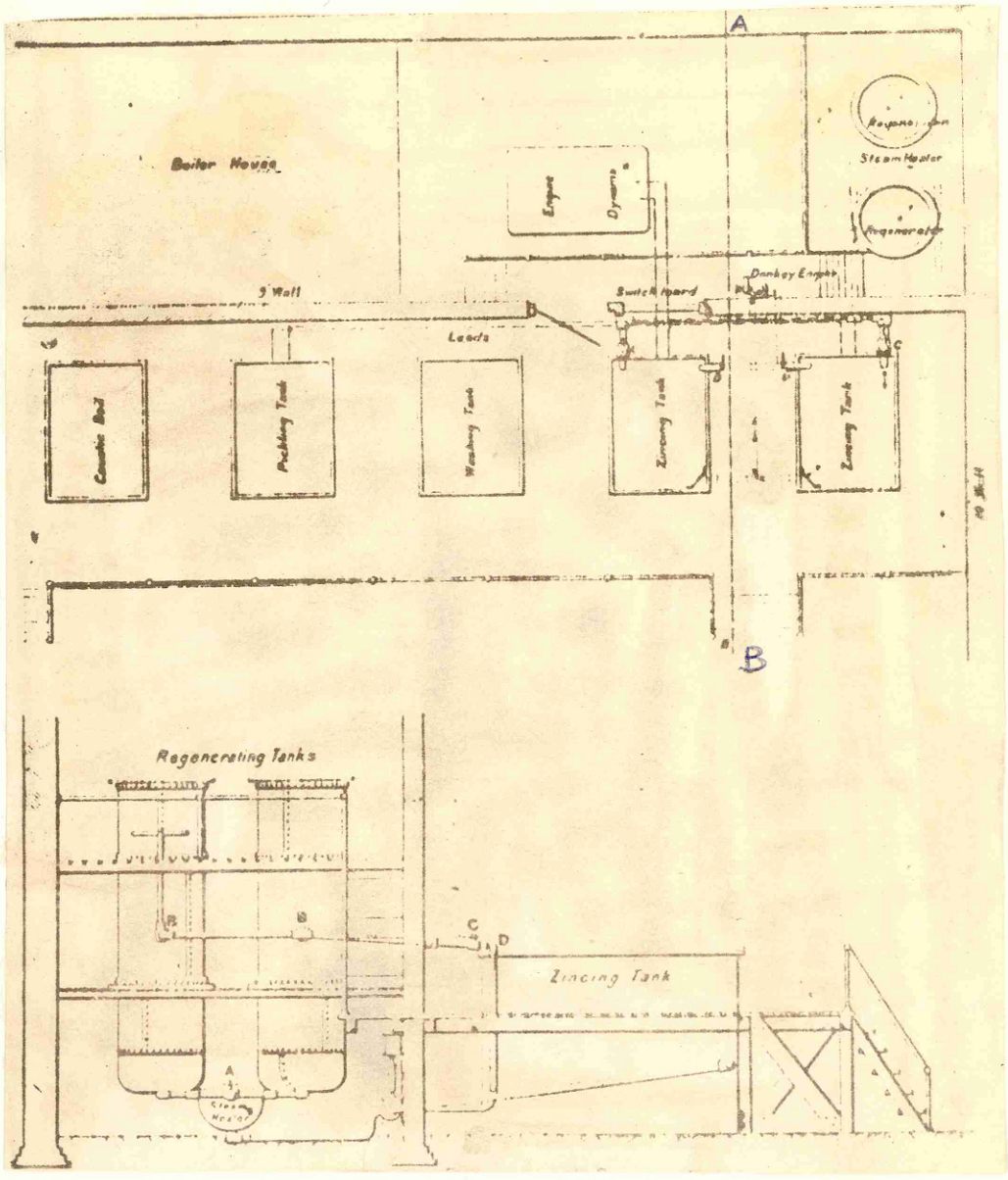


FIG. 117(c) PLAN AND SECTIONAL ELEVATION OF COWPER-COLES' 'ELECTRICAL GALVANIZING PLANT' (375)

These tanks worked either by injectors or pumps. Plants to these specifications were erected for Messrs. Laird Brothers, Birkenhead, the Thames Ironworks and shipbuilding company and Messrs. Mandsley, Sons and Fields' Works.(375)

11.3.9 Electroplating wire with zinc

Both pickling and hot galvanizing have the disadvantage of reducing the strength of wires. By exposure to the lowest working temperature of the hot galvanizing baths, steel wire of high breaking strain was found to have its hardness and consequently its ultimate tensile strength reduced by as much as from 5 to 10 per cent by the drawing of the temper and the formation of an iron zinc alloy on the surface of the steel.

It was the practice, when coating steel wire, to keep the bath of molten zinc at as low a temperature as possible, and to run the wire through at a high speed. But these combined causes led to a considerable waste of zinc by reason of rapid solidification of the metal on a comparatively cold wire, and they also led to the ready breaking or cracking off of the covering metal on bending or twisting, owing to the difficulty with which the molten zinc at low temperature adheres to the steel.

During the nineteenth Century the first successful attempt to electroplate wire with zinc came, following the development of the 'cold galvanizing' process shown in fig. 118, by S. Cowper-Coles.

Up to this time no practical method had been found to produce a wire capable of withstanding more than one immersion in a copper sulphate solution.

By this process wire could be coated with zinc to a thickness of .003 inches, or an increased diameter of .006 inches, capable of withstanding eight immersions in a saturated copper sulphate solution.

Cowper-Coles found that a wire .069 inches diameter with a total thickness of .003 inches of zinc could withstand repeated bending round a bar 1 inch in diameter without exhibiting any signs of peeling or cracking. Fig. 118 shows the type of equipment used commercially at this time.

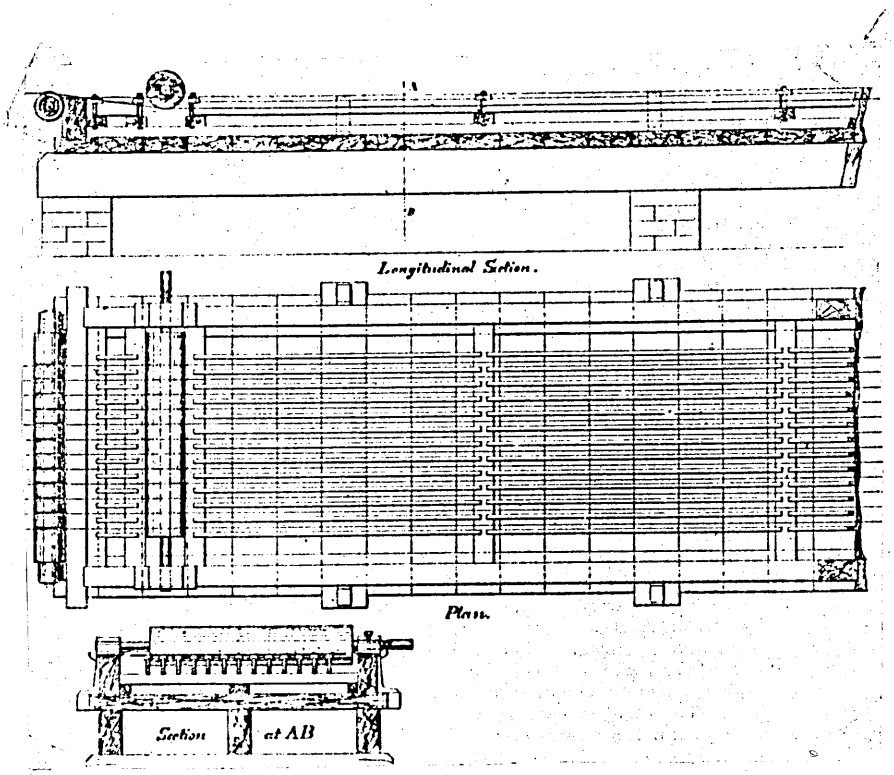


FIG. 118 WIRE GALVANIZING PLANT (375)

The vat for the electrc plating of wire with zinc was constructed of wood and lined with sheet lead.

Wood covers were provided which were faced with lead and fitted with counter weights so that they could be readily lifted for the purpose of cleaning the vat or inspecting the wires under treatment. The covers when in position formed part of the anode, making contact with the ridges, and thus forming a lead anode around each wire. The solution was circulated rapidly through the plating vat and passed into tanks supplied with zinc dust, contact brushes provided with weights or springs, pressed upon the wires in the spaces provided between the covers, "collected the electric current, and at the same time burnished the zinc deposit. Another form of burnisher consisted of rollers which were mounted on carriers capable of turning on centres.

)(378)

The carriers were arranged to turn on guides so as to respond to any uneveness or alteration of wire position. The guides carrying the rollers were pressed together by springs to give the necessary pressure for burnishing.

It is of interest to note that during the development of this technique for applying pressure for burnishing, Cowper-Coles used rubber bands! It was only later that a spring system was introduced.

To economise on space the drums were mounted so as to turn upon a spindle, the lower drums having a flange for supporting the lower coil of wire. Between the drums secured to a spindle, a collar was provided with pins or supports for carrying the upper coil of wire.

CHAPTER 12. SHERARDIZING

12.1 The inception of the process

The process of sherardizing or 'dry galvanizing', dates from 1900 although the principles involved in sherardizing were not entirely unknown previous to this. In 1838 M. Berry[96] took out a British patent in which he coated iron and copper in a manner similar to the sherardizing process. In 1896[97] Roberts-Austen showed that it was possible to alloy gold and lead at temperatures well below the melting point of lead.

Sherard Cowper-Coles produced a zinc coating on iron and steel unintentionally during the annealing of some iron and steel samples while packed in zinc dust. The zinc was being used as a supposedly inert substance for packing in order to exclude the air. Fig. 120 is the only photograph

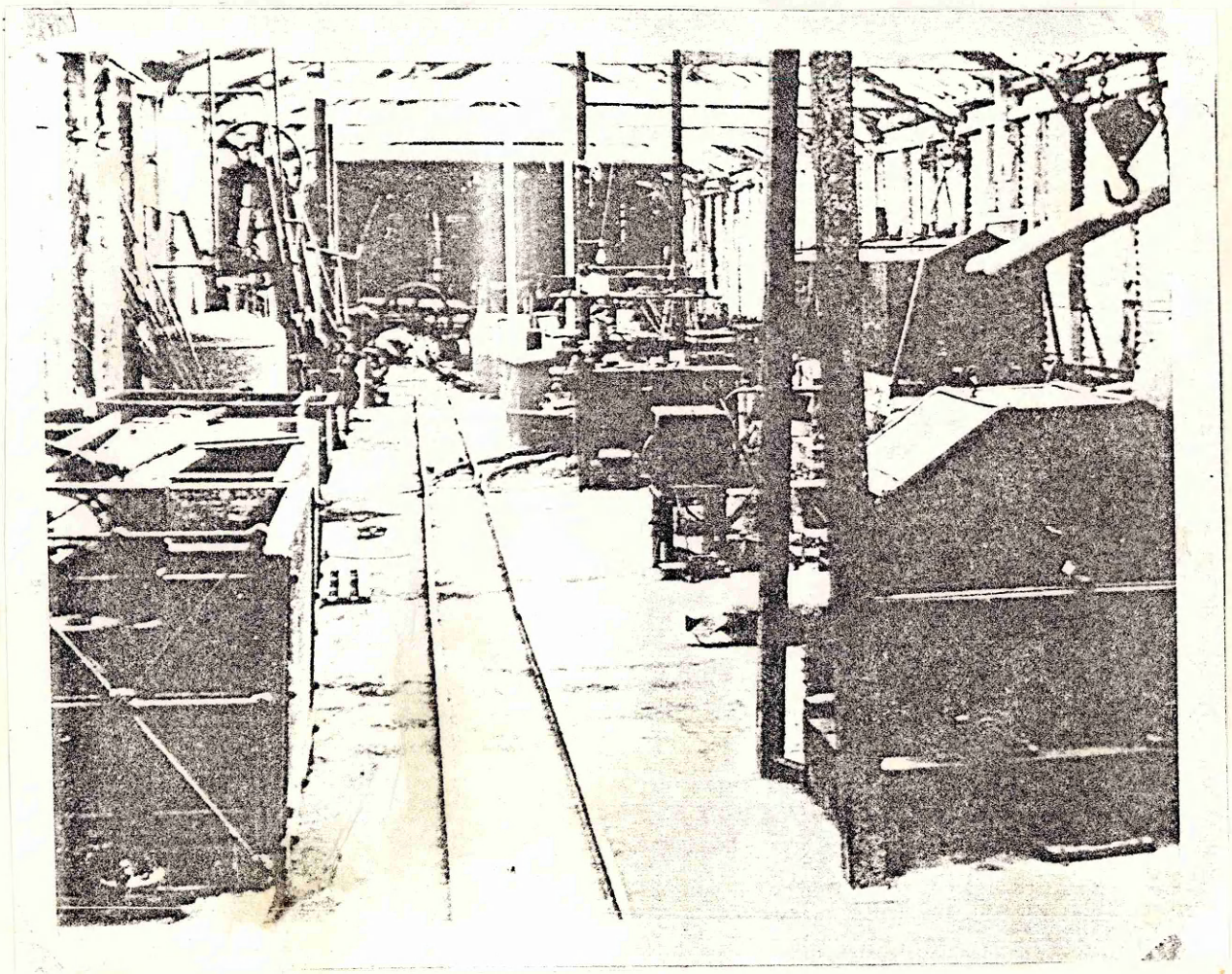


FIG. 119 THE WORKSHOP IN WHICH THE SHERARDIZING PROCESS WAS DISCOVERED AT SUNBURY-ON-THAMES IN 1900.

Acknowledgement to Mr. P.L. Cowper-Coles for loan of original photograph.

Subsequent examination showed that the zinc had not only coated the iron but had alloyed with it and penetrated into the iron surface.

The indication that this was a chance discovery is enhanced if one examines Cowper-Coles methods of investigations.

In a workshop (Fig. 119) adjacent to his home at Sunbury-on-Thames many investigations in a variety of scientific fields were continuously carried out by fifteen scientific workers. There was no planned programme of research. Ideas appeared to have flowed continuously from his fertile mind and his workers were expected to follow whatever whim or fancy he momentarily thought of. To aggrevate the situation even further, many of these instructions were passed into the workshop in a series of notes, with little personal contact. Consequently on many days the workers were peppered with instructions directing them on one scientific adventure and then onto another, until confusion prevailed. The salaries of the workers were rather low and they were not organised into any form of trade union. At least one of the workers must have thought of him with particular affection. At the age of 55 he married this lady and she complemented him with much of his work.

These are the circumstances and conditions under which "sherardizing" was born. It was not the result of many years careful scientific analysis into cementation but a chance discovery.

A plaque on the wall of a church incorporating a sherardizing plant in the engraving stands as a permanent memorial to his discovery (Fig. 121). The original workshop at Sunbury-on-Thames, after serving a period as a museum (Fig. 122), is now destroyed.

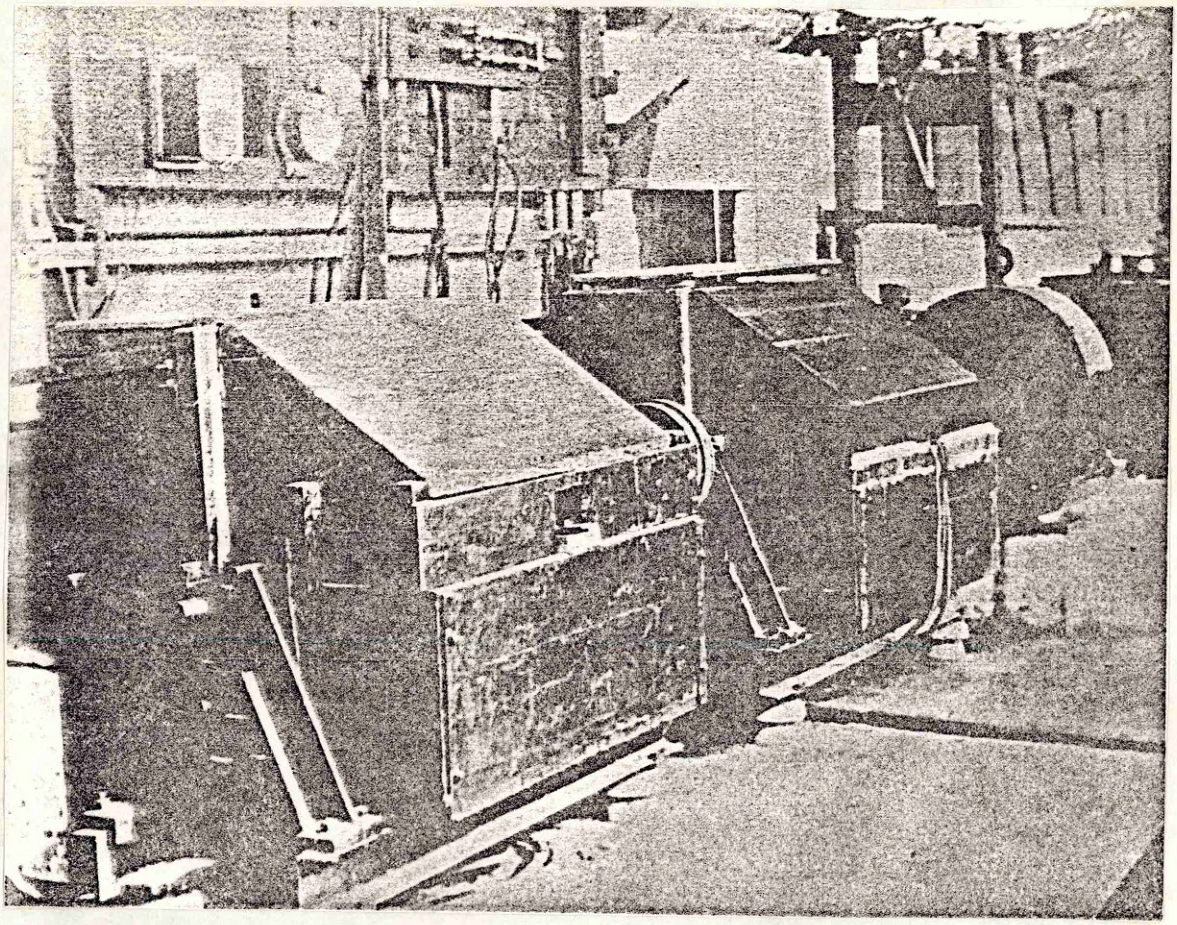


FIG. 120 THE FIRST SHERARDIZING PLANT. THIS WAS LOCATED IN THE SHERARD COWPER-COLES WORKSHOP AT SUNBURY-ON-THAMES.

Acknowledgement to Mr. P.L. Cowper-Coles for loan of original photograph.

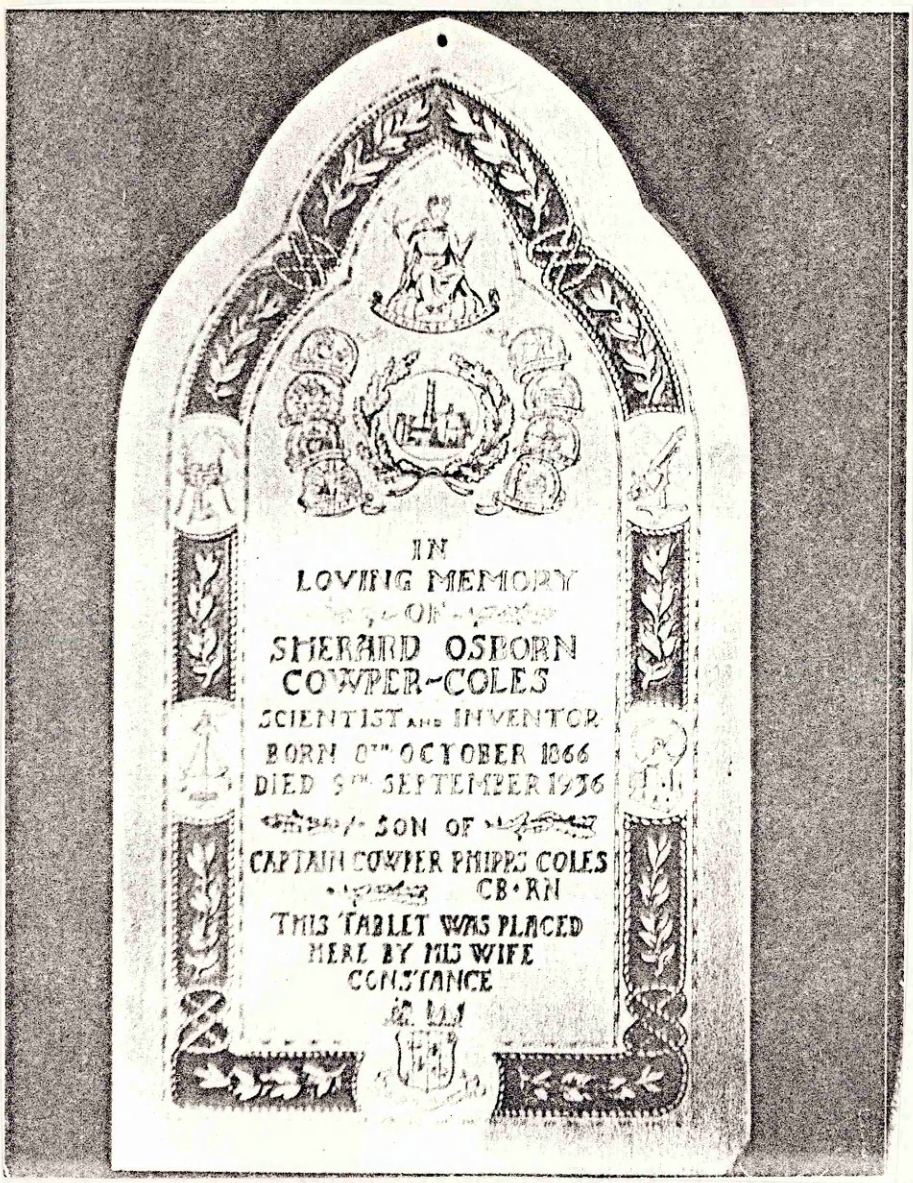


FIG. 121 A MEMORIAL PLAQUE TO SHERARD COWPER-COLES INCORPORATING A SHERARDIZING PLANT IN THE CENTRE OF THE DESIGN. (S. HARTING PARISH CHURCH, SUSSEX.)

Acknowledgement to Mr. P.L. Cowper-Coles for loan of original photograph.

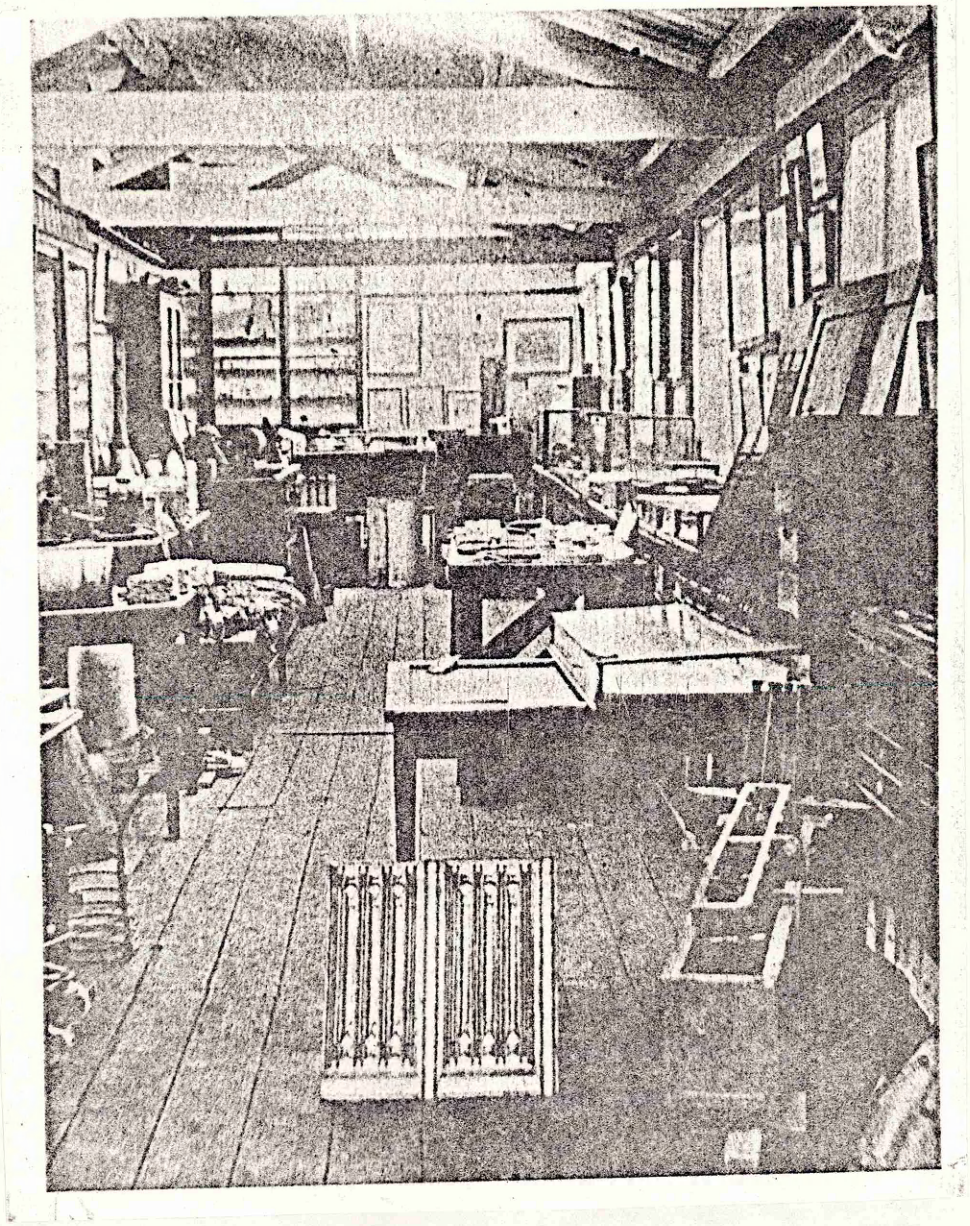


FIG. 122 THE SHERARD COWPER-COLES MUSEUM THAT WAS AT SUNBURY-ON-THAMES.

Acknowledgement to Mr. P.L. Cowper-Coles for loan of original photograph.

12.2 Patent

The original sherardizing patent (ie British Pat. 5647) was taken out in 1900. The rights for America were sold and in 1908 a parent company was formed to control them.

The policy adopted by this company was exactly the reverse from that adopted by the English company and proved very successful. The American company granted licences to firms on a minimum royalty basis. The result was that sherardizing soon became an industry of considerable magnitude.

Johnson and Woolrich noted in 1912 "The Sherardizing process after getting a firm hold in England appears to be spreading in the United States"(377).

12.3 Development of the first commercial Sherardizing Plant

This discovery led to a number of investigations being undertaken, and ultimately a small plant was erected in a workshop at Danvers Street, Chelsea. The apparatus used consisted of a wrought-iron cylinder with an opening at the side for inserting the zinc dust and articles to be sherardized. This drum was heated by a row of gas burners placed beneath it and was continuously rotated.(379)

The trial apparatus proved so successful that a small company was formed, which erected a commercial plant at Willesden. The plant comprised four furnaces capable of taking drums of 8ft x 2ft with a cubic capacity of about 2 tons of material at a charge, varying according to the shape and thickness of the articles to be sherardized.

The charging of the drums was effected by running the truck on which the drum was placed on to a table (fig. 123). One end of the table was lowered by means of gearing, so as to tilt the other end into which the zinc dust was charged from an upper floor by means of a shoot. The drum was discharged, after the sherardizing operation had been carried out, over an iron grating, allowing the zinc dust to fall into a chamber below from which it was raised by means of a chain elevator to the floor above.

When the drum was charged with zinc dust and the articles to be sherardized, it was brought into a horizontal position, the air exhausted and

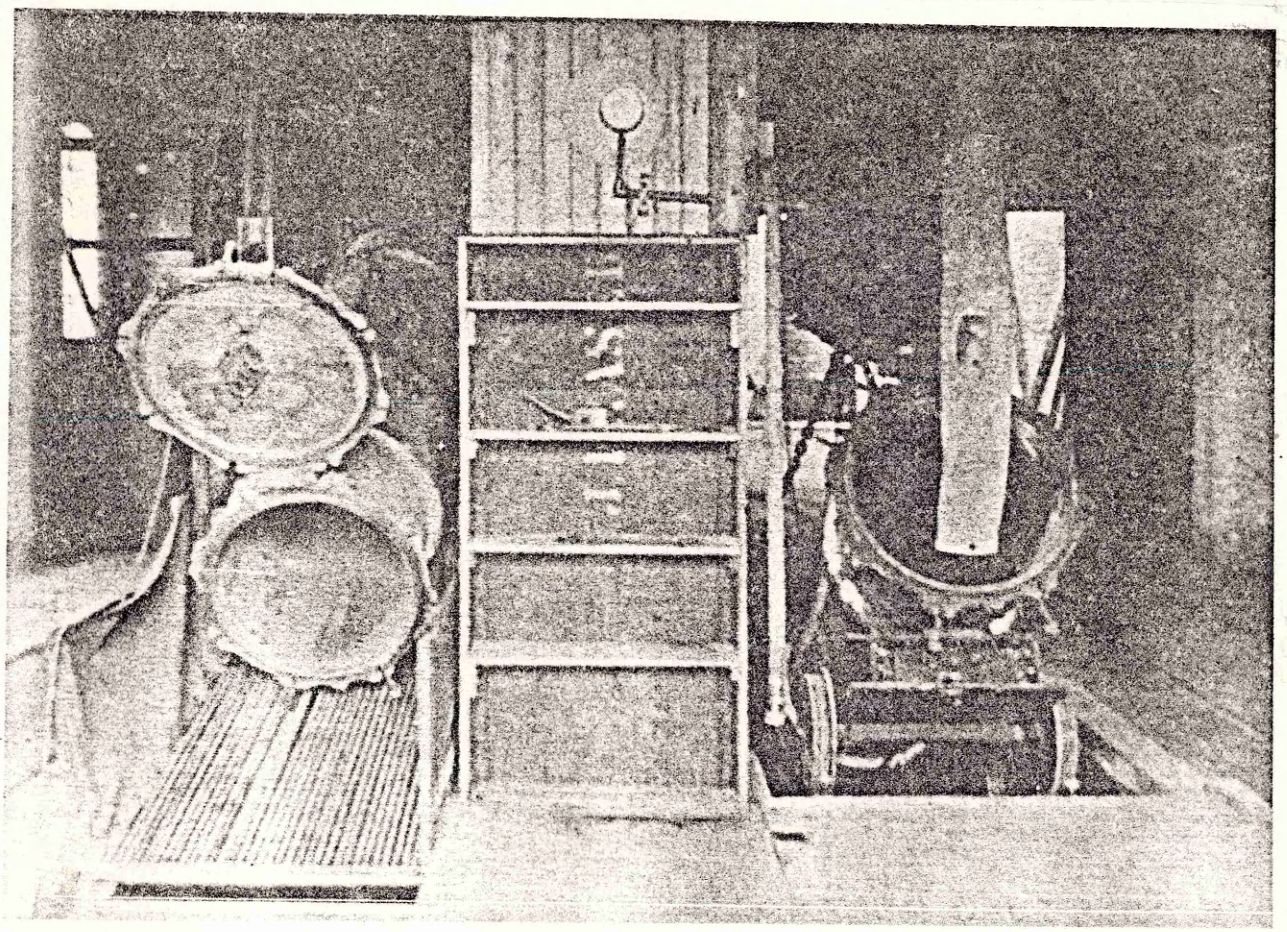


FIG. 123 ORIGINAL WILLESDEN PLANT. (379)

the drum and under-carriage ran along the rails until it arrived in front of the furnaces. The drum was then lifted on to a furnace under-carriage, the object being to effect a saving in the first place, in the cost of the under-carriages and secondly to save heat.

The drum was then pushed into the furnace, the door lowered and the furnace heated up to the desired temperature. The heat was regulated in accordance with the readings of a thermometer which was placed in a horizontal iron tube inside the drum, through one of the trunnions which was hollow. When the drum had been in the furnace a sufficient time to give the desired result, the door was raised and the drum and under-carriage withdrawn. The drum was lifted on to another under-carriage and run into an open yard where it was allowed to cool down to a temperature low enough to admit to easy handling of the contents.

Some good speciments of this finished work can be seen at the Science Museum, South Kensington, London.

12.4 Early misconceptions

Unfortunately when sherardizing was first discovered many extravagant claims were made for the process as is so often done with new inventions.

Sherard Cowper-Coles recalled twenty four years later:[378]

"Many erroneous and misleading statements have appeared in the Press".

As the process came into use there were many disappointments because these extravagant claims were not borne out in practice and as a result the commercial development was slow until the nature of the process was understood and its limitations ascertained. The statement[266] that "the sherardizing process adds nothing to the surface of the article" caused the greatest amount of trouble. The claim was made that "you can take a screw from your watch, sherardize it, and replace it again without rethreading".

Where screw threads were sherardized on this assumption, the indignation and wrath of the manufacture may be imagined when threads came back for recutting. As zinc is added to the surface of the iron due allowance should have been made.

During the first decade of commercial use there was no marked improvement in the quality of sherardized articles.(266) The quality of work produced by various manufacturers was very variable. In some cases the protection afforded, even with a heavy deposit, was small while in other instances thin coatings were practically indestructable under ordinary weathering conditions.

A lack of understanding of the process, especially with the relation of time, temperature and metallic content of the dust in the production of suitable coatings, resulted in several investigators researching into the fundamentals and the nature of zinc-iron alloys.

12.5 Trood's investigations

During the early years after the inception of the sherardizing process virtually nothing was published on the practical aspects.

The first commercial plant had been built two years after the discovery, but with this lack of research into the practical aspects, manufacturers were able to give little advice on the satisfactory operation of the plant in order to give consistent results and also explanations about the basic theory. Consequently good results were only rarely obtained and the process began to fall into disrepute.

It was probably beyond the capabilities of the inventor of the process Sherard Cowper-Coles, to engage in a sustained programme of research into many of the problems. He had been 'educated by a governess in a castle' and had no scientific training. Although a gifted inventor, his interests were legion and he would not have had the patience or time to investigate practical problems that would be involved with the commercial development of the plant.

The first person known to have been directly involved in this sphere was Samuel Trood who was a consultant engineer with a large manufacturing company. He had both the scientific background and the practical experience to investigate the problem.

He recalled(99) "In looking into the details of sherardizing I found mysteries in every step of the process. Today the shop did good work, and

tomorrow, with practically the same methods, the work would not be acceptable. In the same sherardizing drum, one side would sherardize sufficiently, when the other side of the drum would not start to sherardize at all".

The plant[379] was installed for the purpose of sherardizing material for their own product. The material included bolts, nuts, malleable iron castings and line material which could not be satisfactorily treated by other methods.

Trood carried out a full investigation and found four major problem areas which he consequently solved. These can be classified as follows:-

12.5.1 Environmental problems

The sherardizing plant had been installed in the same room with pickling and hot galvanizing. The steam and acid fumes from the large pickling tanks (used for pickling large castings preparatory to painting) were consequently found to have a deleterous effect when in contact with zinc dust. A delay period also was noted between the pickling operation and washing, resulting in a thin coating of rust forming on the surface of the metal.

12.5.2. Equipment problems

The clutches which connected the drums with the driving mechanism were crude and clumsy so that they could not be applied from the outside. This necessitated the cooling of the ovens to allow a workman to enter to attach a clutch.[98]

Considerable trouble had been encountered by the dust caking and balling in the drums. They found that this became so difficult at times that nearly a whole drum of work would be scrapped and a lot of dust wasted. This condition was practically eliminated by confining the dust in a bin away from all water or acid vapours, as well as keeping the temperature within the limits for the particular dust used.

12.5.3 Black spots on finished work

One of the principal difficulties was the elimination of black spots on the finished work.[98] At times they became very excessive, not only detracting from the appearance of the work but also reducing the number of dips the material would stand under test. They found two principal causes for this fault. The first was the presence of "burnt in" slag in the corners or crevices of the material which it was almost impossible to remove by pickling in some instances. This was corrected by more intelligent inspection of the material both before and after pickling. It was found that the material received practically no inspection before treatment. Whenever slaggy material reached the sherardizing department, the inspector was notified and it was often found that the material had been removed from the foundry more than two years before. Trood introduced an entirely new system of inspection resulting in the elimination of black spots from this cause.

The second cause was the presence of acid in the spongy or porous parts of a casting which was not thoroughly washed or neutralised. They found it difficult to obtain castings without some porous parts or corners that were filled with fine cracks but by careful attention to pickling and neutralizing, the black spots were reduced to a minimum.

12.5.4. Non uniformity of coating

For no apparent reason different thicknesses[379] of coating were produced, even with the same material and under the same conditions. A heat analysis of the furnaces however showed a variation of temperature. This was found to effect the uniformity of the coatings considerably, although the drums were rotated throughout the run.

The fault was corrected by putting new baffles in the furnaces, additional heat insulation on the doors and new burners which gave more uniform distribution of heat.

Trood encountered some difficulty in the case of one particularly malleable iron article or cqp which was wedged on the end of a wooden rod.

The sherardizing had to be done before the iron cap was formed on the rod. Whenever the sherardizing was heavy this forming process would cause cracking or peeling of the coating. By increasing the temperature and decreasing the time of the process (using blue dust) the quality of the coating was greatly improved.

CHAPTER 13

PROTECTIVE OXIDE FILMS

13.1 INTRODUCTION

During the latter part of the nineteenth century industrial processes were developed to produce adherent oxide films on steel as a means of protection against corrosion.

Passing observations were made by Brande and Faraday (SEE Ref. 380) in 1861 during the course of some experiments on the superheating of steam in iron tubes. They found that the iron became covered with a closely adherent coating of magnetic oxide and that this covering prevented the metal underneath from undergoing oxidation.

13.2 BARFF INITIATES FIRST PROCESS

A method based upon this action was introduced by Barff in 1876.[41][42] This was the first occasion that an attempt had been made to utilise this protective film in a practical way and a degree of success was obtained. In his specification[41][42] Barff described the process as follows:-

"In carrying out my invention, I place the objects composed of iron and steel in a muffle, or chamber, so constructed that it may be in part closed, and so that the contents of the interior of such muffle or chamber may be raised, by means of external heat, to an elevated temperature, and when the objects or articles have acquired a temperature sufficiently elevated to cause the decomposition of steam or aqueous vapour when brought into contact therewith, I inject the same, and continue the action of the steam, or the aqueous vapour, until the desired protective film or coating of the oxide has been produced."

Fig. 124 represents the experimental apparatus used by Barff in his primary investigations.

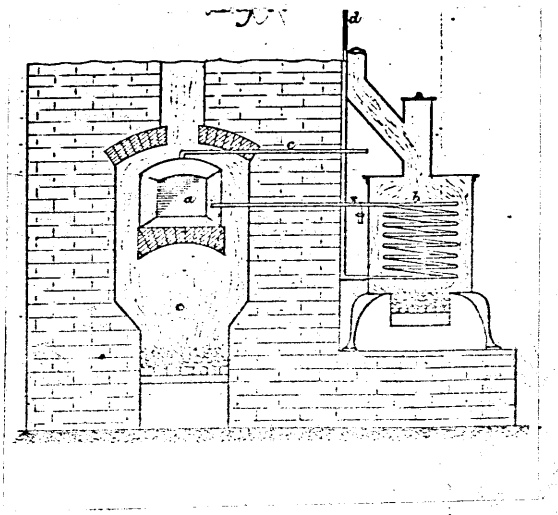


FIG. 124 FIRST APPARATUS EVER USED FOR PRODUCING A MAGNETIC OXIDE FILM. (Fe_3O_4) (41)(42)

"a" treating chamber, "b" coil steam generator and superheater, "c" furnace, "d" water supply pipe, "e" hydrogen escape pipe.

Fig. 125 represents the commercial equipment subsequently adopted by Barff.

It can be seen that the muffle "a" was in this instance a brick chamber beneath which was fixed an ordinary fire grate "b". The heat of this fire passed both under and around the brick chamber and so to the chimney.

Alongside this chamber was a steam generator "c", beneath which, and directly over the fire grate "d", was placed a coiled steam superheater "e", from which the steam, highly superheated, issued direct into the brick chamber or muffle.

The hydrogen, the result of the decomposition of the steam, was led by the pipe "f" to the underside of the fire grate, where it was consumed.

Barff later mentioned in 1879[43] in the opening paragraph of an article on The Treatment of Iron to Prevent Corrosion:-

"It is now more than two years ago since I had the honour of introducing to your notice in this room a process for the prevention of corrosion in iron, and it was through the Society of Arts that it was first made known to the public....."

13.3 BOWERS PROCESS

Following the publication of this work there followed an article in the Times Newspaper describing the process.[381]

It was this second report that was seen by a George Bower of St. Neots in Huntingdonshire and was to stimulate him and his son Anthony into many

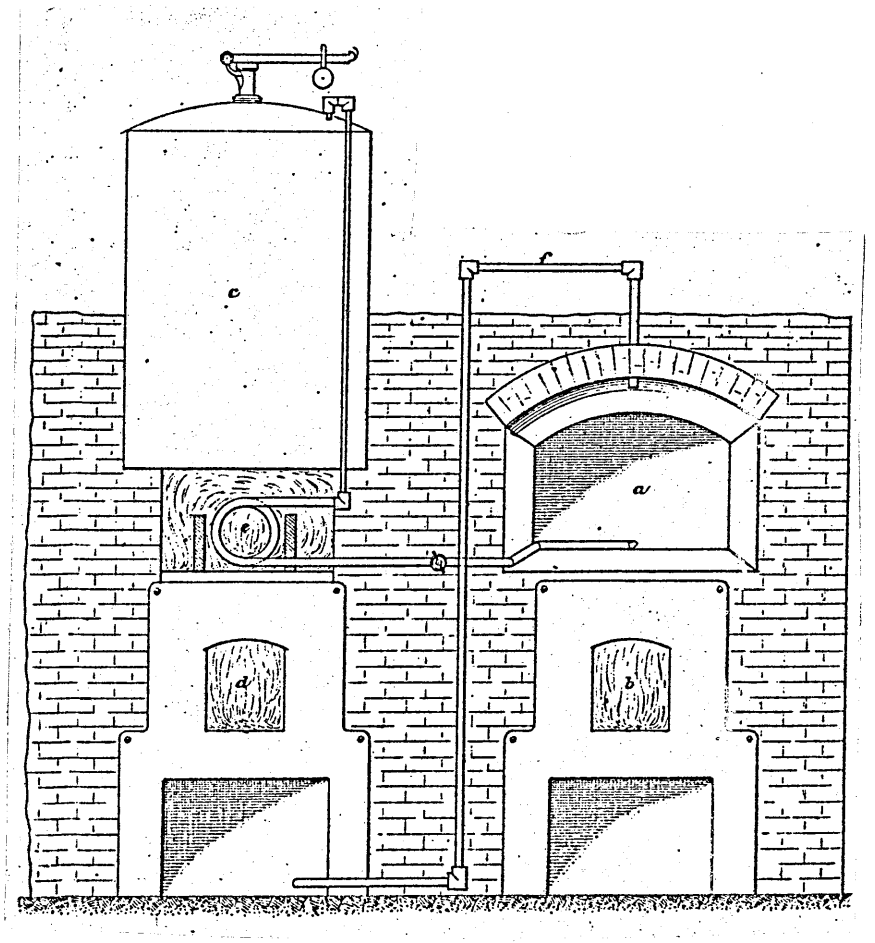


FIG. 125 ('PRACTICAL') EQUIPMENT LATER USED BY PROFESSOR BARFF (43)

years activity modifying and perfecting the practical applications of the process.

Anthony Bower later wrote:-(51)

"Upon reading a description of the Barff process in the London Times, it occurred to my father that what the professor could effect with steam he might also effect with air, and several experiments were made to this end, which were very varied in character, as were also the results obtained."

George and Anthony Bower were the key figures in making a commercial success of the process.

George Bower was born in Caistor in Lincolnshire and in the 1871 census he was described as a Gas and Water Works Contractor at St. Neots. His son Anthony at that time was 19. The 1877 Post Office Directory indicates that apart from his business in St. Neots, he also had connections with the Milton Ironworks, West Hartlepool. The 1916-28 edition of Who was Who indicates that he also had another son George who would have been at Winchester College as a scholar at about that time. He later became a prominent barrister.

The intellectual ability of George (Jnr.) was matched in equal measure by the ingenuity of his brother Anthony. For although George (Snr.) initiated the investigations of this new process, the major credit for the development was given by the father to his son.(44)

Following the 'Times' article George carried out a series of experiments with air as an agent and a sample of iron. He consequently found that the iron had a most adherent coating of magnetic oxide. The first furnace device for carrying out the air process consisted of an externally heated chamber, in which the iron articles to be treated were placed. When the iron had attained the temperature of oxidation, a few cubic feet of air was blown

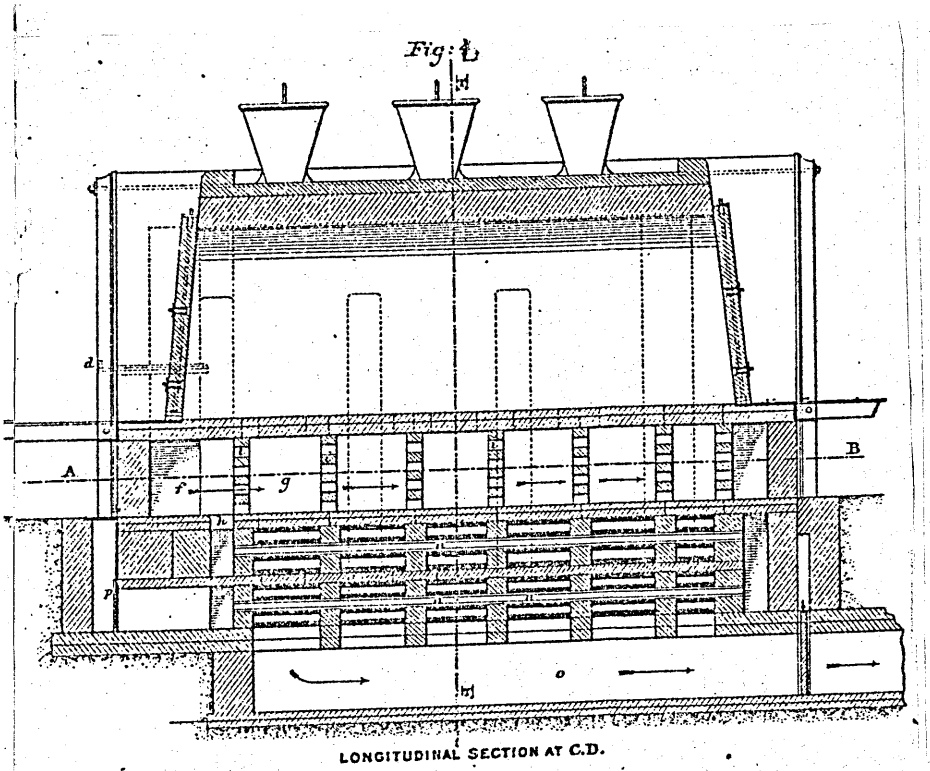
into the chamber which had been devised. The iron entered into combination with the oxygen in the air and a thin film of magnetic oxide was formed on the metal. Fresh air was admitted occasionally to replenish the oxygen appropriated by the iron, until the requisite thickness of oxide was attained.(47)(48)

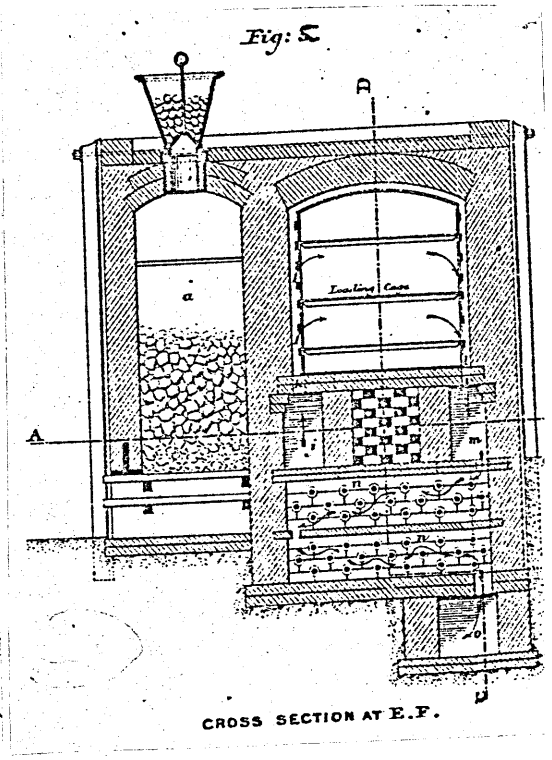
The difficulty and expense of the application of external heat were so great that it occurred to Anthony Bower, who was conducting experiments, that if the internal application of heat could be substituted and the coating of magnetic oxide produced simultaneously with the action of heating, by a series of oxidising and deoxidising operations, the process could be simplified considerably, be more effective and far less costly.

Elaborate experiments were conducted with this aim and the results far exceeded their expectations.

Figs. 126 (a), (b) and (c) represent plans and sections of the furnace used. The combustible gases were generated in the three producers 'a' and passed over the partition walls 'b', descending by the down cast 'c', in which was fixed a regulating valve 'd'. The gas then passed along the horizontal flue 'f', to the mouth of the combustion chamber 'g', where it met the current of heated air ascending from the recuperators by the port 'h'. Combustion, mixing and oxidising of the gases was attained by the series of intercepting chequer walls 'i'; the products of combustion descended from the muffle by the ports 'e', into the side flue 'm', passing then into a recuperator and by going round the air tubes 'n', of fire clay, they transmitted their heat to the air flowing to support combustion. The products of combustion then escaped into the chimney flue 'o'.

In the Trans. Am. Inst. Min. Eng.(51) Anthony Bower gives an account of these series of experiments with carbonic acid (carbon dioxide) chemically produced by the decomposition of chalk.





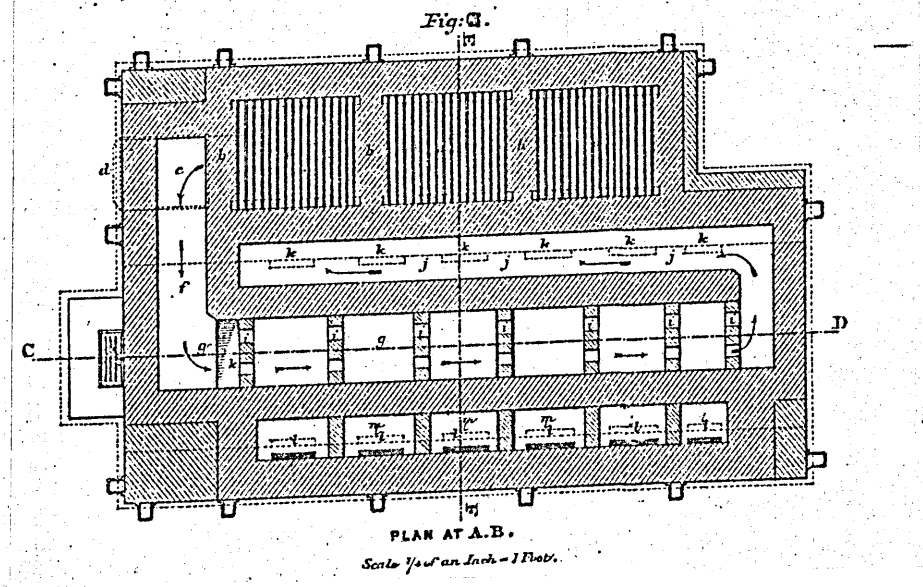


FIG. 126 FURNACE USED BY GEORGE AND ANTHONY BOWER FOR PRODUCING MAGNETIC OXIDE FILMS (Fe_3O_4) (47) (48)

"In these experiments something quite different was obtained, inasmuch as the coating was very light in colour, pleasing to the eye, but easily removed. The idea was that three equivalents of iron would unite with four of carbonic oxide, forming one equivalent of magnetic oxide and four of carbonic acid, if the heat was sufficiently high. This reaction expressed symbolically thus:-

$$3\ Fe + 4CO_2 = Fe_3O_4 + 4CO \quad \text{- - - - - - - (2)}$$

"..... I increased the quantity of free oxygen mixed with the products of combustion, and oxidised the iron articles to excess during a fixed period of generally 40 minutes, when magnetic oxide was formed close to the iron and Fe_2O_3 over all. Then for 20 minutes I closed the air inlet entirely, leaving the gas valve open, and so reduced the outside coating of ferric oxide to magnetic oxide by the reducing action of the combustible gases alone. The excess of oxygen in the first instance produces Fe_2O_3 and the under surface of this, being in contact with metallic iron, undergoes reduction to magnetic oxide in the following manner: Four equivalents of ferric oxide unite with one of metallic iron, forming three equivalents of magnetic oxide, or symbolically:

$$4\ Fe_2O_3 + Fe = 3\ Fe_3O_4 \quad \text{- - - - - - - (3)}$$

When deoxidising by combustible gases, consisting mainly of carbonic oxide, three equivalents of ferric oxide unite with one of carbonic oxide and form two equivalents of magnetic oxide and one of carbonic oxide:

$$3\ Fe_2O_3 + CO = 2\ Fe_3O_4 + CO_2 \quad \text{- - - - - (4)}$$

Another reduction is by carbon itself:-

$$3\ Fe_2O_3 + C = 2\ Fe_3O_4 + CO \quad \text{- - - - - (5)}$$

"..... Equation (4) is also the reaction when rusty iron is reduced by producer gases, which consist largely of carbonic oxide and by the specimens exhibited it will be seen that articles completely pitted with rust may have their surfaces rendered rustless. In this case the

periods of oxidising and deoxidising are reversed - the latter occupies 40 and the former 20 minutes. No oxidising is theoretically necessary, but practically a certain amount is requisite to keep up the heat in the chamber."

13.4 BARFF & BOWER PROCESS COMPARED

From the date of his discovery in 1876 Barff took an active interest in perfecting the process until the end of the decade.

From fig. 125 it can be seen that the Barff process required an external application of heat to the muffle which if this was to be of any considerable size would be costly. In addition a seperate steam boiler and a seperate superheater were required. In all, three distinct operations were necessary.

For ordinary cast iron containing more carbon than mild steel the Barff process was slow in its action. However, for wrought iron and polished steel the Barff process was found to be more suitable since the Bower process was found to be much too energetic in its action and wrought iron was found to scale.

In general terms, the Barff process was on several accounts more costly than the Bower process but for some applications was superior.

13.5 BOWER - BARFF PROCESS

By the end of the decade the patents for the Barff process had been purchased by George Bower.

It could be that Professor Barff as an academic was not particularly interested in the commercial exploitations of this process once the principles had been established and perfected to the best of his ability.

George Bower being an industrialist and having a son as a very

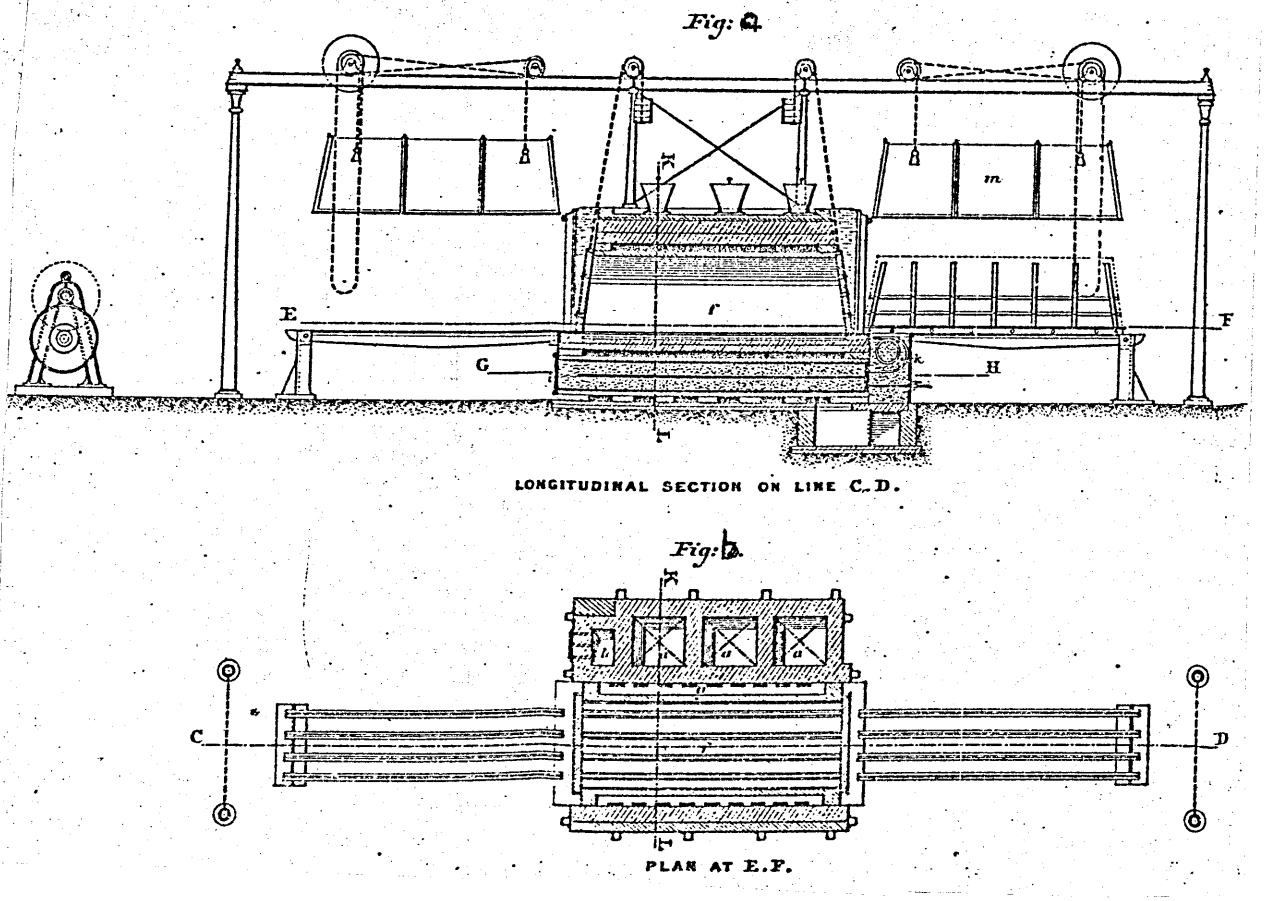


FIG. 127 THE COMBINED BOWER-BARFF FURNACE USED FOR PRODUCING MAGNETIC OXIDE FILMS. (49)

interested party, decided to incorporate the best features of both systems and commercially develop the process.

One of the main features of the new system appears to have been a reconstructed furnace.(49) The advantages of both the original Bower and Barff processes were incorporated together and it was then possible for both cast and wrought iron to be coated with ease.

The furnace which the Bowers developed, which incorporated the best from both systems, was used for many years.

It is shown in fig. 128 'a' are the three gas producers; the gas generated was passed over partition or dividing walls descending by the downcast 'b', where its flow was regulated by damper 'c'. The air to support combustion entered by the regulating air inlet valve 'd', and combustion took place at the point 'e'. The flow of products of combustion could be directed over the muffle 'f', by the side flue 'g' and then turned into the chimney flue, or by withdrawing the damper 'h' directly on to the steam superheater 'i', or by closing the damper 'h' and withdrawing the damper 'j', the products of combustion could be directed immediately on to the steam superheater, without having to be passed over the muffle.

Difficulties were experienced in perfecting the process and were echoed by Anthony Bower.(50)

"..... The development of the process has been a long and tedious business, and one requiring much faith and patience of most disheartening failures for months together ....."

B. H. Thwaite, an employee at the company, also related the problems:-(382)

"..... In the preliminary experiments great difficulty was found in obtaining a satisfactory and durable form of steam superheater. Circular coils of lap-welded steam pipes were first tried, but although effective as superheaters, their cost and liability to stoppage, the necessity of frequent renewal and the rapid oxidation of the wrought iron, were grave objections. In order to prevent the oxidation of the casing its outer sides were grooved, to retain a refractory lining of a mixture of silicate of soda and fire clay; but this lining soon commenced to crack and flake off on continuous exposure to the flame....."

Thwaite in his deliberations continues to highlight in detail the problems that they faced in the successful development of the process.

The form of superheater finally adopted is illustrated in Figs. 127 and 128 and rolling carriage in Fig. 129.

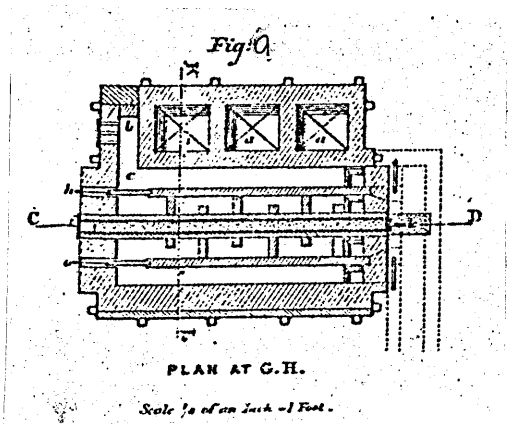
The main advantages of the Bower - Barff process appear to have been the ability to protect intricate parts and also that of providing a good base for paint work.

13.6 FILM LIMITATIONS

By the year 1881 the processes developed by Bower and Barff had become well known in the scientific world in general.(383)

The moment of truth came at a meeting of the Iron and Steel Institute early in that year. By this time it was the Bowers who were the champions of the process; Barff having sold his patents some time before.

It was a Mr. E. Riley(52) at this meeting who was able to spotlight and foresee what one of the major problem areas was going to be in the application of the process. Nearly everybody present at the meeting was in full



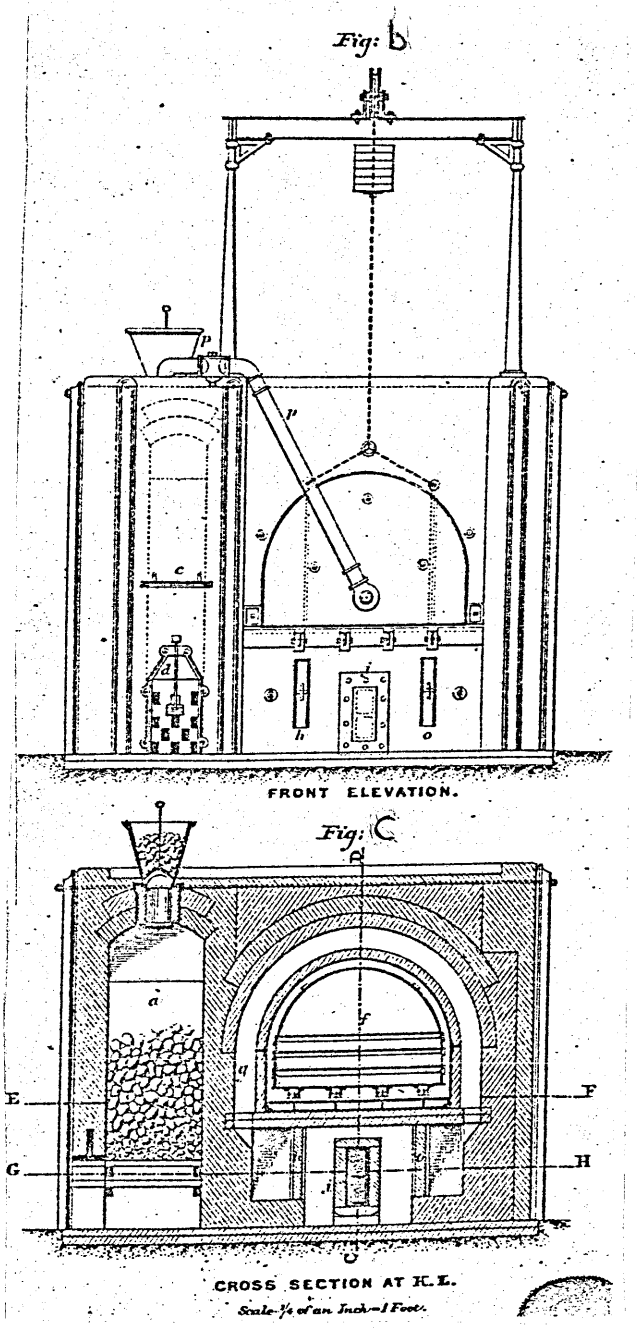


FIG. 128 THE COMBINED BOWER-BARFF FURNACE USED FOR PRODUCING MAGNETIC OXIDE FILMS. (99)

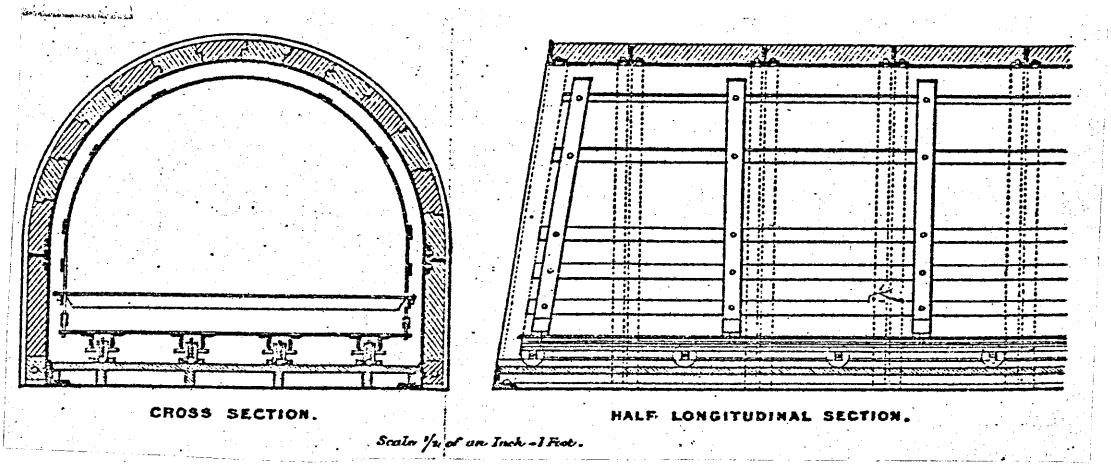


FIG. 129 DETAILS OF THE ROLLING CARRIAGE USED BY BOWER FOR TRANSPORTING MATERIAL INTO THE FURNACE.(99)

praise. His judgement was later proved to be correct, resulting in a considerable limitation in the application of the process, although within these confines it proved valuable service for many years.

Any manipulation or accident that injures the continuity of the covering surface must necessarily lead to accelerated corrosion since the protection of the metal depends upon the fact that the metal is electropositive to the coating.

Riley in his discourse stated:-(52)

"..... I would like to put it to Mr. Bower, supposing they had to drill holes in angle iron, and assuming that a girder was covered with the magnetic oxide, it was clear that iron will be exposed where the bolt went through. It seems to me that the angle iron and the bolt not being coated with the magnetic oxide, there must be great chemical action due to the formation of a galvanic current. There would be serious difficulty in other places where the magnetic oxide was removed."

Riley was able to appreciate that because the anodic area was small the anodic current density at that position would consequently be high and result in rapid corrosion. Equally important was the fact that Riley did not choose an abstract example to illustrate the problem, but one that would be very meaningful to a practising engineer.

However, G. R. Tweedie in a discussion on this point actually thought that localised corrosion was an advantage:-(53)

"..... The peculiarity of having magnetic oxide on the surface of iron was this: If they broke away the surface they found that the rust was confined to that spot. There was no tendency to 'lateral' rusting, as in the case of painted surfaces. There was a great advantage in this respect

over other methods of protection, for although the oxide might be chipped in places, corrosion was strictly localised."

The protection given to iron by a magnetic oxide coating is good providing there is no break whether due to coating imperfections or the result of mechanical action.

It is of interest to note that in virtually none of the tests carried out on specimens under a variety of environmental conditions and which gave good results, mechanical action such as drilling or machining had taken place.

The Silver Light Company of Whitecross Street, London stated in 1879 in a letter to Barff:-(383)

"We have subjected lamp stands to exposure in a damp place and on examining them at a later date we could trace no alteration in their appearance....."

A Letter to Prof. Barff from Messrs. Warner Hydraulic and Sanitary Engineers from Cripplegate, London stated:-(384)

"..... The closet pan which you covered for us we have exposed to the atmosphere for a period of four months and subject to frost, snow, rain and smoke, yet we do not see the slightest appearance of rust....."

It was on the basis of claims of this specific nature that Barff made a universal claim for his process.

13.7 AMERICAN & CONTINENTAL DEVELOPMENTS

While the development of the process continued in England, considerable interest was being shown in America. In England a non-coking gas coal was employed and the first furnaces in America were designed for this fuel. However the price of coal there at that time proved to be a serious drawback to

its continued use.

Bower and a Mr Winslow, who was experimenting with the process at the Heda Works, New York, decided to substitute anthracite and petroleum for bituminous coal. Petrol was allowed to trickle through a small pipe at the rate of about one gallon per hour upon the red hot surface of the coal in one of the gas producers. They found it especially advantageous because just at the right period it furnished a large volume of reducing gas. The petrol was found to be very beneficial because of the degree of control it was possible to have. When it was necessary to raise the temperature of the furnace in a very short time, sawdust, together with anthracite was successfully employed.(55)

In England the finishing treatment for castings had been in successive oxidation and reduction operations. Winslow decided to use superheated steam. It was found that after the last reduction the admission of the superheated steam for a period of 1 - 2 hours was very advantageous. It re-oxidised any over reduced coating and ensured a coating of constant quality, besides giving a fine lustre. A low temperature was required for obtaining good results with polished work, wrought or cast.

A charge of polished ware was put into the furnace at red heat and the metal absorbed the heat and reduced the temperature. The combustion chamber and regenerator were found to maintain a high temperature and effectively superheat the steam before it reached the iron in the furnace chamber.

Polished work treated in this manner and then dressed with flower-emery and oil, had a coating of blue-black lustre. This treatment was not needed for ordinary iron for which the operation was carried on at a higher temperature and in relatively shortened time.

Articles which were to be exposed to active rusting influence were

treated for 7 - 9 hours, whilst those for indoor use received only a very thin coat in an operation which lasted from 2 - 4 hours.

Winslow, who developed this plant, took the precaution of avoiding the treatment of both very light and very heavy articles in one charge. He appreciated the problems of the 'mass effect' at a time when this was not widely appreciated in England.

If he wanted to treat both polished and iron material at the same time, he applied plaster to the polished surface. Plaster of Paris was also applied in thick coatings to protect the screw threads of bolts, gas pipes, etc. from an energetic process of oxidation. A thin, but perfect coating was found to be formed beneath the plaster - which was ample to protect threads.

The process was carried out in Belgium by Van Aubel, Engineer of the Maestricht Royal Paper Factory. He treated several articles and then exposed them to the fumes of the laboratory without any deterioration.

Flamache, Engineer of the Belgium State Railways, found that concentrate hydrochloric acid diluted to 1/10th the concentrated strength converted the magnetic oxide into sequioxide which dissolved. A solution of caustic soda was found to have no effect on the coating. Cracks in the coating resulted in the exposed metal rusting, but this was found to be localised. He also claimed that the rustless treatment did not alter the strength of the iron. This fact was also noted by Sir Joseph Whitworth (44) in England who carried out a series of tests after exposure.

Flamache also found that under tensile or compressive strains the oxide adhered firmly to the iron until the limit of elasticity of the metal had been reached. However the oxide was easily chipped off the metal by hammer blows.

George Bower, refering to Flamache, mentioned that he was sent over from Belgium specially to report on the process by their Public Works Department. He was particularly interested in the cost aspects of the process and suggested during this visit to St. Neots that a saving could be made by having one workman attending several furnaces and by having one gas producer for several chambers.

13.7.1 Gesner Process

The next major process following Bower-Barff was the Gesner process in 1888.(385)

While the Bower-Barff process formed a magnetic oxide coating, in the Gesner process the surface of the metal was changed into a "compound of hydrogen, iron and carbon" which had a lesser tendency to scale off than the magnetic oxide. It was less brittle and more elastic. A claim made for the coating(386) was that the dimensions of the articles treated, screw threads and nuts were not greatly enlarged; while the Bower-Barff process if not carefully controlled gave large size increases.

The material which was to be treated was placed in a retort and treated to 600°c, this temperature being maintained for about half an hour. Low-pressure steam which had been partially dissociated into "hydrogen and oxygen" by being passed through a red hot pipe in the bottom of the apparatus, was then allowed to act at intervals on the iron for a further half hour, after which there was introduced into the retort a small quantity of hydrocarbon oil, the details of which were not given. This was given fifteen minutes to act and carbonate the surface of the metal. The main principle of the process appears to have been identical with that of the Bower-Barff. The time of the treatment being less in the Gesner process than by Bower-Barff to get the same thickness of coating. This probably accounts for the claim for the process of having less danger of warping.

Figs. 130, 131 and 132 illustrate what Gesner called a hydrogen generator.

It was stated that:-(387)

"A large variety of iron and steel goods have been already treated in quantities by the South Brooklyn Rust Proof and Steel Works, among them being builders and art hardware, roofing shingles, stove fittings, pipe and pipe fittings, parts of water meters, steam radiators, pistols and other articles. The colour produced is a dark blue. The process was also described in the Journal of the Iron and Steel Institute.(388)

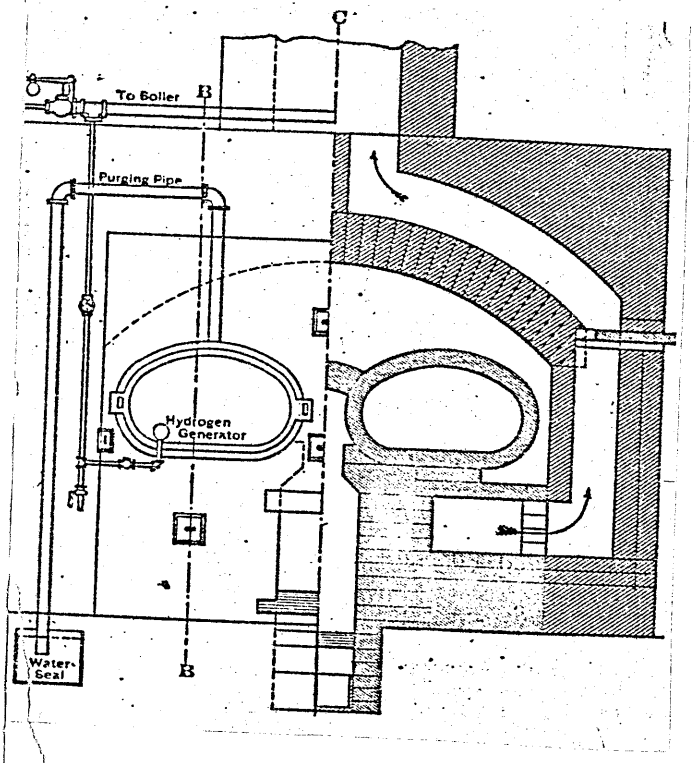
In 1897 Gesner patented a process for producing an "alloy of iron and hydrogen"(389) which he described as resisting oxidation and corrosion, being capable of "working like iron and being nearly the same strength, but of somewhat lower specific gravity." Hydrogen was blown through iron in a converter, 1,000 cu. ft. of hydrogen at 60° was found to be sufficient for 2,000 lb. of iron or steel; the temperature of the metal was to be 2,800°f; and the depth 15 in.

In 1900 he took out a further patent on the alloy which is formed as a scale by the action of the hydrogen on hot iron;(390) the hydrogen to be produced by the decomposition of steam and the scale was to be crushed, ground and sieved for purposes not specified.

13.8 OTHER PROCESSES

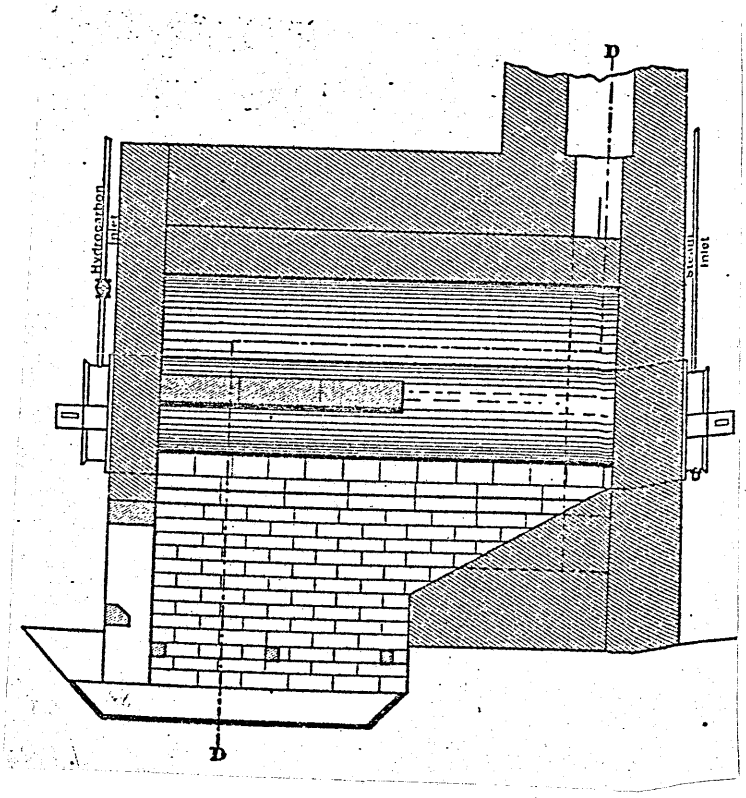
A process was patented by W. D. Wood(391) in which sheet iron was subjected to the action of hydrogen vapour or gas and superheated steam within an airtight and heated chamber. This was very similar to the Gesner process.

In Platts' process a flexible coating of black oxide was given to iron wire, the wire had first to be in an oxidised state and was then submerged in oil. (392)



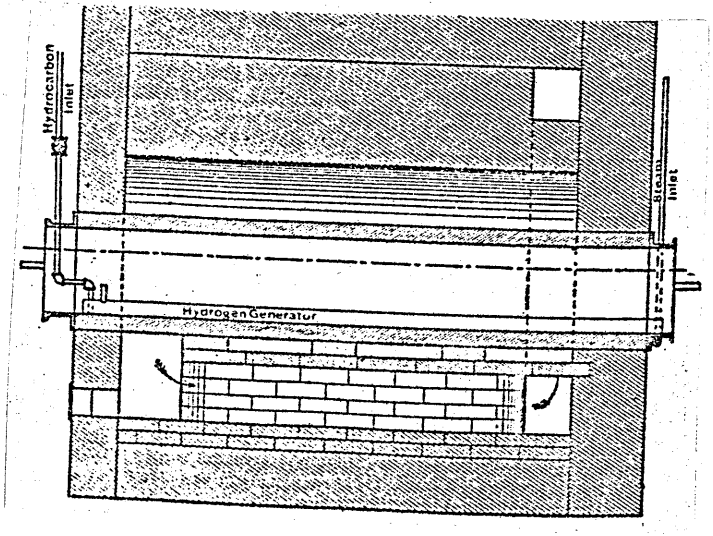
FRONT ELEVATION SECTION THROUGH DD

Fig. 130



SECTION THROUGH CC

Fig. 131



(c) SECTION THROUGH BB

Fig. 132

THE GESNER FURNACE

A variety of processes[393][394][395][396] were considered in the wake of the Bower-Barff developments, but none of them survived the test of time by producing consistently good results which is the main prerequisite for any commercial success.

CHAPTER 14

ALLOYS OF STEEL

14.1 INTRODUCTION

There are many elements in an alloyed combination with iron; some are present as 'impurities'and there are those which are added to confer specific properties to the material to improve either the mechanical or corrosion resisting properties or both.

The alloys which are considered in this section are those which are known to have better corrosion resisting properties than those of basic iron or steel,and were developed in the nineteenth century.The alloys themselves were not primarily developed because of this feature and indeed this factor may not have been considered as of great importance at the time.

In this section the contribution of the elements is traced where possible from its discovery through the time period of the first beneficial observation to the time when it was examined in a systematic way and its corrosion resisting properties either determined or compared with other alloying elements.

The alloys that were examined were those which were found to have good mechanical properties.

14.2 CHROMIUM

The metal chromium was claimed to have been discovered by Vauquelin in 1797.[397] He stated that the then new metal,of which samples were exhibited before the Académie des Sciences,was white,brittle, crystallised in needles and that acids had very feeble action upon it.It was this property of resisting,particularly acids,that was to be of such great importance well over a century later.The name "chrome" was suggested from the salts of the metal, being of a characteristic colour.It was in Vauquelin's paper[397] that the term "chrome" was first used.

Faraday,in addition to his researches in the electrical field, devoted considerable time and energy to the study of iron alloys and in[33] 1820 he published his work 'Alloys of Steel' in conjunction with J.Stodart

In this paper he stated that his purposes in proposing these experiments on the alloys of iron and steel with various other metals was two fold:-"first,to ascertain whether any alloy could be artificially formed,better for the purpose of making cutting instruments than steel in its purest state;and,secondly,whether any such alloy would under similar circumstances,prove less susceptible to oxidation."(33)

Although in this work Faraday and Stodart were more interested in producing alloys of greater strength,they observed that alloys of iron and nickel had little evidence of rusting,yet alloys of steel and nickel appeared to accelerate rusting.In this respect they gave no details of the experiments of percentages of iron and steel used.

However in alloys of platinum and steel,they do quote a percentage of 90% platinum and 10% steel as being an alloy which did not tarnish.

This article was given good coverage in the Continental journals.(34)(35)

A further paper was published in 1822 on the 'Alloys of Steel'(36) by Faraday and Stodart.During this period in his career Faraday also tried to obtain a non-corrosible metal for reflectors.He alloyed iron with chromium,and might well have produced 'rustless steel' nearly a century before it was actually marketed,had he continued this line of investigation. Like his earlier article,this was given wide coverage on the Continent.(37)(38)

Following the publications of these reports,although Faraday made periodic references to alloy steels at later times,he never produced any major papers on this topic.This could have been because Stodart,who was skilled at preparing the metals for him,died shortly after the publication of the second report.Faraday's interests may then have turned to other problems.

Following the publication of Faraday and Stodart's earlier article(33) Berthier undertook a series of experiments on alloys of chromium and iron or steel.In this article he stated(398) that he had spent a lot of care on

the preparation of ferro-chromium, not solely because he believed such material had in itself special value, but because he believed it would be found as a means of introducing chromium into cast steel. Unfortunately in this work Berthier did not carry out any specific experiments to determine the corrosion resistance of the ferro-chromium alloy. However it is of interest, that Berthier mentions that the idea of introducing chromium into steel was suggested to him by Faraday.

Although Berthier mentions this, Mallet in his paper in 1838[399] before the British Association, gives Berthier the credit. Probably the original idea and some experimental work which was carried out by Faraday had been taken a step further by Berthier.

In an interesting side to this, in 1924, Armstrong stated in the Proceedings of the American Society for Testing Materials:-[400]

"Boussingault calls Berthier the inventor of chromium steels. It seems, however, that Boussingault overlooked the interesting article before the British Association in 1838"

In fact it was the author of this article himself who had not properly read the 1838 article since it stated there that Berthier was the inventor.

Experiments with the metal then appear to cease until 1857[401] but these, like so many other investigations, ignore corrosion resistance aspects apart from a passing mention of the metal's insolubility in the presence of concentrated acids.

Baur took out an American patent in 1865[402] claiming " A steel greatly improved, toughened and hardened by the addition of chromium and also suitable for making steel practically." There was no mention about any claim for protection against corrosion. He made many investigations and gave some practical applications of chromium steel, but the first introduction of the steel for use in industrial purposes was probably due to Brustlein, of the Holtzer Company, who paid special attentions to this particular alloy. Brustlein commenced his experiments in France in

1875, and his firm, Holtzer, first supplied chromium steel for industrial purposes in 1877.[403] Brustlein admitted that he was led to make his own experiments from seeing an account of Baur's work in America.

Investigations were also carried out at this time on the Continent on the production, constitution and properties of chromium steel by Boussingault, but nothing extensively new was introduced.

A book was published in 1890 on the Metallurgy of Steel[404] In this Howe gives a good résumé of the metal chromium and its application to steel. In this work, as in nearly all the other papers that had been published, there was no reference to any experiments comparing the corrosion resistance characteristics of the material.

The first systematic research presented as to the effect of chromium alloyed with iron in varying percentages was published as a small part of a paper by Hadfield in 1892[39]

Between 1890 and 1892 Hadfield made a series of alloys of iron and chromium varying from 0.22% up to 16.74% chromium, comprising a range of 15 alloys. In seven of these alloys the carbon present amounted to 0.21% or under; in five of them the carbon content was from 0.4 to 1.00% and in the remaining three was from 1.27 to 2.12 % carbon.

Detailed information was given in this paper concerning the method of manufacture, composition, forging, heat treatment, mechanical and physical properties, microstructure and other particulars.

It was in this paper, that the subject of the corrosion of chromium steel was first dealt with in detail.

Hadfield found that high chromium steel, for example, specimen 'L' mentioned in the paper containing 9.18% chromium, was quickly corroded or eaten away by sulphuric acid. He was, therefore, the first to show that alloys of iron with high percentages of chromium would be of little value under this particular test.

(39)
Accompanying this paper to the Iron and Steel Institute was a

report by the French metallurgist, Professor F. Osmond, who was a friend of Hadfields.

In his conclusions regarding the chromium steel, Osmond stated that "--- as the amount of chromium increased, a compound of iron, chromium and carbon appeared to be formed, which was only partly attacked by acids and possessed great hardness."

As a result of the researches of Hadfield and Osmond, important information was obtained in the development of chromium steel of various types. These contributions, by Hadfield and Osmond, were the first records demonstrating that the resistance of chromium-iron alloys varies with the nature of the attacking acids.

The steel does not appear to have been developed any further at this time. This is possibly due to difficulties in obtaining suitable chromium or ferro-chromium of the required low carbon type at a price which would have enabled industrial products to be manufactured.

14.3 NICKEL

Nickel appears to have been mentioned first of all by Hierne in 1694.[406] He spoke of a mineral containing nickel, commonly known as 'Kupfer-nickel'. It was originally considered to be a species of cobalt or arsenic.

The first recorded experiments on nickel used in alloy steel were carried out by Faraday about 1820.[33] At this time Faraday carried out a number of experiments on different alloying metals with a view to obtaining better cutting tools. He used an alloy of 3% nickel at first and found that it was a great improvement over plain carbon steel. This nickel was present along with the iron in 'iron' that he obtained from Artic regions.

This 'iron' that Faraday used, and which by chance contained a quantity of nickel could have been the impetus that Faraday had for investigating further the effect that nickel had on the strength of the material.

Not only did Faraday investigate the strength of the material he also observed the effect of corrosion.(33)

"--A piece of this alloy (10% nickel) has been exposed to moist air for a considerable time, together with a piece of pure iron; they are both a little rusted, not, however to the same extent; that with the nickel being slightly acted upon, comparatively to the action on the pure iron; it thus appears that nickel, when combined with iron, has some effect in preventing oxidation."

Mallet in his report to the British Association in 1838(407) placed Nickel fourth in the 'order of corrosibility', after chrome, silver and gold, when alloyed with steel. However he makes no further comment about it.

Like chromium, the interest in Nickel was centred around the increased strength that it bestowed on iron and steel, and for nearly fifty years investigators appeared to ignore any corrosion resisting properties that it may have had.

In 1889 Riley read a paper before the Iron and Steel Institute, entitled 'Alloys of Nickel and Steel'(408) during the course of which he pointed out that samples of steel, rich in nickel had been lying exposed to the atmosphere and under his observation for several weeks, nevertheless they still exhibited an untarnished fracture. He further described a series of experiments in which samples of nickel steel were immersed in dilute hydrochloric acid.

Compared with mild steel with a relative percentage of 100%, 5% nickel steel had a relative corrosion of 83, and 25% nickel steel had a relative corrosion percentage of 1.15.

Six years later, Wiggin gave(409) the results of a series of experiments in which the relative losses in weight of 3% nickel steel and 'open hearth Bessemer' steel were determined in two different ways:-

1. Polished specimens of steel were immersed in 10% salt solution in flasks, maintained for a period of three months at boiling point, pure

water being added at intervals to replace that lost by evaporation.

2. Similar pieces of steel were submitted to the action of steam at atmospheric pressure for two months.

At the conclusion of the experiment the Bessemer Steel had a relative corrosion of 181% in salt water and 215% in steam compared with 3% nickel steel. 'Open hearth' steel had a relative corrosion of 197% in salt water and 115% in steam compared with 100% for 3% Nickel. The results indicate that under conditions of steam, the 3% Nickel steel has only slightly better corrosion resisting properties than the open hearth steel.

A comprehensive investigation to determine the corrosion resisting features of the iron-nickel alloy was carried out by Hadfield in 1899.[410] He tested a range of alloys with various Nickel contents ranging from 0.95 to 29.07 % in 50% concentration of sulphuric acid. The weight loss after 21 days is recorded in figs. 133 and 134. From this, and other data, it is possible to compare the corrosion resistant features of these alloys with those steels with other alloying elements (Fig 133 and 134).

14.4 COPPER

Although Mallet[399] mentioned that copper alloys were less likely to corrode than iron, F. H. Williams, as late as 1900 appears to have been one of the first to show in a quantitive manner that a small percentage of copper increases the resistance of iron to corrosion.[411]

Hadfield in his comprehensive investigations into alloy steels in the last decade of the nineteenth century never considered copper additions. Corrosion resisting properties were very much a side line in all Hadfield's investigations. His main interests were the development of high strength materials. Copper was well known not to produce these properties, and consequently it was passed by in his investigations.

Nevertheless, when corrosion resisting properties are being considered the copper bearing steels are prominent.

Williams[411] exposed samples of Bessemer steel containing varying quantities of copper to the atmosphere for about a month, during

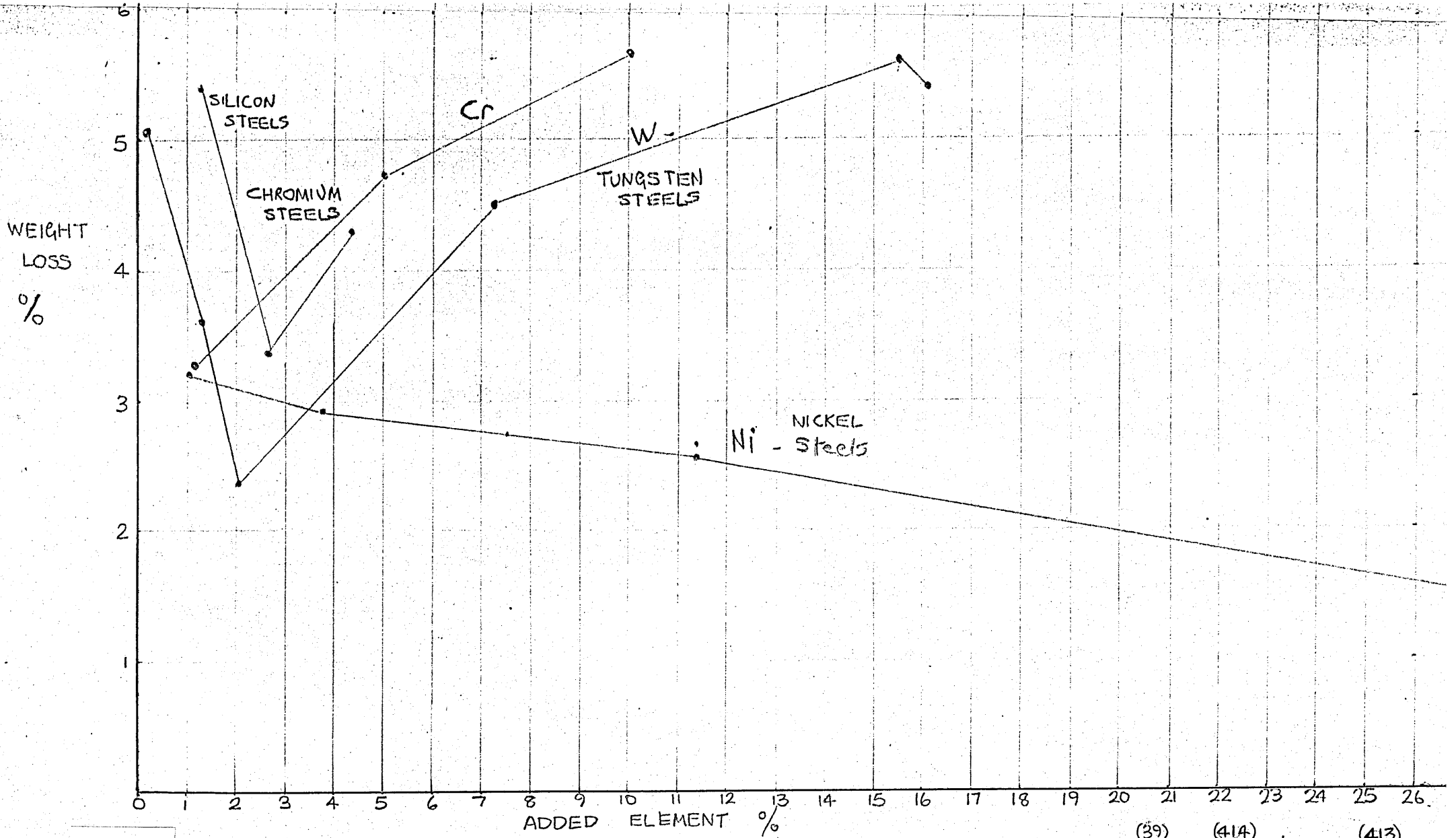


FIG 133 SUMMARY OF RESULTS FROM HADFIELD'S 3 PAPERS IN 1892[39], 1899[414] and 1903[413]

SPECIMEN	C	Si	S	P	Mn.	Ni	Cr	W	MATERIAL	IN 50% H_2SO_4 GRAMS LOSS	IN 50% H_2SO_4 % LOSS	
B	0·15							0·20	FORGED	3·055	5·01	
G	0·21							1·49	"	2·162	3·50	
H	0·28							3·4	"	1·392	2·25	
I	0·38							7·47	"	2·797	4·50	PARTICULARS
L	0·76							15·65	"	3·920	5·75	EXTRACTED
M	0·78							16·18	"	3·574	5·50	FROM
LOW. M. STEEL.	0·40								"		3·97	R. HADFIELD'S
MILD STEEL	0·25								"		2·09	PAPER ON
NICKEL-IRON ALLOY	0·16								CAST		1·37	"ALLOYS OF IR
PLATINOID									"		0·35	AND TUNGSTE
METALLIC CHROM.									"		·03	J. Iron & Steel
METALLIC MANG.									"		10·60	Inst.
NICKEL									"		VERY SLIGHT.	1903 (413)
IRON								99·8	"		4·52	
CHROM. STEEL F	0·27						1·18		FORGED		3·32	EXTRACTED
" J	0·77						5·19		"		4·78	FROM.
" L	0·71						9·18		"		5·64	R. HADFIELD'S
SILICON STEEL E	0·20	2·67							"		3·32	PAPER ON
MILD STEEL S									"		7·48	"ALLOYS OF
WROUGHT IRON									"		*44·7*	IRON AND CHROMIU
												J. Iron & Steel Inst. 1892 (39.)
1287 C	0·13	0·23			0·72	0·95			CAST	2·003	3·23	EXTRACTED FR
" E	0·19	0·20			0·65	3·82			"	1·611	2·95	R. HADFIELDS
" G	0·17	0·28	0·11	0·08	0·68	7·66			"	1·581	2·77	PAPER ON "ALLOY
" I	0·18	0·22			0·93	11·39			"	1·390	2·60	OF IRON & NICKEL
" M	0·14	0·38			0·86	29·07			"	0·759	1·34	Proc. of M. Inst. of Civil (414)

which period they were soaked with water several times daily. He worked on a less percentage. For soft Bessemer Steel this value was 1.85% and with additions of 0.263% copper was 0.74%. The addition of this copper reduced the corrosion rate by more than a half.

Stead and Wigham[412] obtained similar results for iron wires containing copper. They weighed portions of the wire and placed them side by side in wooden frames and immersed them in a tank through which a constant stream of water circulated. After a period of nine weeks the wires were removed, cleaned and weighed. The cupriferous steels were less corroded than the steels without copper, the maximum resistance being obtained with 2% of copper.

14.5 TUNGSTEN

Elhuyar was the first to discover tungsten in 1792, but it was not until the midnineteenth century that tungsten was first introduced as an alloy to steel and became very valuable in the manufacture of high speed cutting steels. An essential requirement being that cutting steels must retain their strength, toughness and hardness at a high temperature. There appears to be only one reference to the corrosion resisting properties of this alloy and this was in a paper published by Hadfield in 1903.[413] Only a very brief reference was made yet tests carried out were done in a systematic manner. (Fig 133 and 134.)

14.6 SILICON

For many years chemists had been familiar with the fact that the presence of silicon tended to retard the corrosion of iron.

Mallet was aware in 1838[407] that cast iron rich in silicon was not readily attached by acids. However nothing further appears to have been published on the corrosion resistant properties of silicon and iron until a paper published by Hadfield in 1889,[414]

A comprehensive set of experiments were carried out comparing this steel with others in 50% sulphuric acid, for 21 days. These are illustrated in fig 133 and compared with other alloys on fig. 134.

14.7 INFLUENCE OF OTHER ELEMENTS

Although little experimental evidence is available on the alloys already mentioned there are very few isolated facts to be gleaned from the writings of investigators as to the action exerted by some of the other elements upon the corrosibility of iron.

Calvert and Johnson[415] prepared an alloy of aluminium and iron by heating a mixture of lime, aluminium chloride and iron filings. The resulting product was very hard and rusted on exposure to damp air. Analysis showed that it contained 12% of aluminium.

Faraday and Stodart[36] found that alloys of iron and platinum containing 11% of platinum were highly resistant to oxidation, exhibiting no corrosion after several months exposure. They found that an alloy containing 50% rhodium was capable of resisting corrosion for a considerable time.

Percy stated[416] that cast iron containing about 9% tin was very corrosion resistant.

14.8 EARLY TWENTIETH CENTURY DEVELOPMENTS

In a paper entitled "Stainless Steels" read before the Midland Institute of Mining, Civil and Mechanical Engineers on 8th April 1922, Hatfield stated that it was in "1912-1913 that Mr Harry Brearley discovered that the 12-14% chromium steels, when in the hardened condition, resisted successfully general atmospheric and many other active influences which led to corrosion."

In the intervening years there were no major developments in this field apart from alloy steels of both nickel and chrome which Hadfield stated in a paper published in 1915[417] as" A special alloy known as 'Stainless Steel' has recently come before the Metallurgical world."

This dates the introduction of stainless steel at about 1915. The impetus for its development was possibly in connection with the war effort.

With regard to the tungsten steels, the effect on tungsten of sulphuric acid is practically negligible, although when warm there is a slight reaction. From the graph (fig. 133) 2% tungsten additions appear to be the only suspect result although in the case of this element it is difficult to say whether these results are correct or otherwise.

It is now known that the addition of nickel to iron consistently increases the resistance of steel and iron to sulphuric acid. This is illustrated well by Hadfield's results. The graph shows that as the percentage of nickel is increased then the weight loss due to corrosion decreases. Summarising the sets of the results for the three ranges of alloy, only the chromium additions produced erroneous results and it may be borne in mind that this was the first of the three series he experimented with and his experimental expertise in this field of testing would have been limited at that time.

14.9 ANALYSIS OF PUBLISHED RESULTS

Fig 133 illustrates the importance of completing as many tests as possible before publishing results and drawing conclusions from them. Although Hadfield's paper on 'Alloys of Chromium and Iron' dealt to only a very minor degree with the corrosion resistant properties of the alloy he came to an erroneous generalization that chromium impaired the corrosion resistance of steel in 50% sulphuric acid. Sulphuric acid is a corrosive media in which the 'stainless steels' are close to the borderline between passivity and activity and this is particularly so with chromium steels. It is now known that additions of chromium increase the corrosion resistance of alloys.

CHAPTER 15

OTHER PROTECTIVE SYSTEMS

15.1 OILS, FATS, PAINTS AND VARNISHES

Although the Romans had methods of protection against corrosion using white lead, gypsum of melted pitch, [11] it was not until the nineteenth century that a variety of practical methods was developed specifically for protection against corrosion.

A report in Dingl. J.[56] in 1822 appears to be the first mention in the nineteenth century of the application of varnish. It stated that pieces of steel should be smoked first and then coated with the best quality varnish.

A few years later in 1825 under the heading of 'Noble Inventions' a report in the London Journal of Arts stated[418] that a naval officer in the French Service employed a composition of resin and olive oil, well mixed with ground bricks to protect a water carrier from rust. It mentioned that this had been used by the French Navy to protect iron hoops.

15.1.1 First Systematic Testing

The first comprehensive series of tests on various paints and varnishes was carried out between 1838 and 1840 by R. Mallet (fig. 135)

He stated:-[419]

".....The paints and varnishes were mostly such as are generally in use, and were laid with great care on the cast iron, so as to cover the whole surface completely, and leave as few microscopic pores as possible in the covering. The general results are these : of the ten sorts of paint or varnishes tried, there is not one that will completely prevent corrosion, nor one that will remain perfectly adherent or undecomposed for a single year under water. In foul water, fresh or salt, white lead paint perishes at once, the white lead probably converted into 'sulphuret' (sulphide) by the action of the nascent hydrosulphuric acid; yet white lead forms the great staple base for all the paints generally used for exposed iron works. Caoutchouc (India-rubber type) varnishes appear to be the best covering

No.	Sort of covering, and how applied.	Result in 3 months, on plates wholly submersed.	Result in 3 months, on plates half in air and half in water.
1.	Coal tar, laid on hot; plate heated.	Perfectly preserved, and free from rust.	A few dots of rust at the level of the water.
2.	Thetsee varnish of Ava: two months to dry, first in cool room, and then in a stove, one coat.	Perfectly uninjured in appearance.	A line of rust at the level of the water.
3.	Dhuna, a native varnish; applied to the iron hot, in a thick uneven coat.	White and pulverulent; soft and easily rubbed off while wet; rust here and there.	Large cracks from the contraction of the part exposed to the sun; whitened where thick; black where thin; plate preserved above water.
4.	Best white-lead paint; 3 coats; allowed to dry and harden for 3 months, nearly.	Almost wholly disappeared, and blotches of rust on the surface.	Paint uninjured above water-mark, and plate preserved; but below water entirely removed.
5.	Copal varnish; 2 coats, dried rapidly.	Whitened, pulverulent, and soft, but not much oxidated.	In air less whitened; spots of rust breaking out everywhere.
6.	Spirit varnish; several coats, warmed.	Whitened, and very rusty.	Very much corroded.
7.	White wax; melted on the surface.	No trace of wax left, and very rusty.	This plate was all under water.
8.	White wash of pure lime-water.	Flaky, peeled off, and very much corroded.	In air remains on, and acts pretty well.
9.	Zinc; an edging or guard soldered round the plate when cleaned.	The clean iron exclusively corroded and bad; the zinc also oxidated.	Much more rusty in the air than under water, where a sort of crust had formed.
10.	The iron plate untouched, and covered with the usual gray oxide, as it came from the rolls.	The natural surface was a little whitened, and pretty well preserved.	Rusty on the edges, or where it had been scraped, elsewhere little injured.

FIG. 135 THE FIRST COMPREHENSIVE SERIES OF TESTS ON PAINTS AND VARNISHES UPON IRON. (419)

in hot water, and generally in all the others asphaltum varnish. But boiled coal tar, the iron being hot, has decided advantages over every other....."

Although in this report Mallet stressed the importance of completely covering the surface, it is suprising that no comment was made about surface preparation prior to covering.

During the series of investigations that Mallet carried out, there was a rapid increase in the use of iron ships. Consequently there was considerable pressure on Mallet, as one of the leading experts in the field of corrosion and corrosion protection, to devise a method of protection.

He introduced a method(420) which involved the application of three coatings. The first was a zinc-mercury alloy coating, the second, an organic coating and the third an anti-fouling paint.

From his description he mentioned that the plates were pickled washed, scoured and immersed in a liquid composed of equal parts of a saturated solution of zinc chloride and of ammonium chloride. They were then immersed in a molten bath of zinc-mercury, containing 1.5% mercury to which had been added 0.005% sodium.

This appears to have been the first time that a proper surface preparation process had been introduced.

The completed hull of the vessel, which was entirely coated with zinc-mercury alloy including the rivets, was then covered with varnish made as follows:- 50 pounds of asphaltum(asphalt), 16 lbs. of red lead and litharge in equal proportions, and 10 imperial gallons of linseed oil were boiled together. In a separate vessel, 8 pounds of gum anime(resin) 2 imperial gallons of drying linseed oil, and 12 pounds of caoutchouc softened by coal tar naptha were melted. The contents of the latter vessel were then added to those of the former and the whole boiled until 'tough and ropy'. When cold, it was thinned with 30-35 imperial gallons of turpentine.

For the last operation, a thick paint was made with drying

linseed oil, red lead and barium sulphate, and a little turpentine. To every 100 pounds of the paint, there was added 20 pounds of copper oxychloride and 3 pounds of a mixture composed of (hard yellow soap), melted with an equal weight of resin and a little water. The purpose of the resinous soap was to give the paint a slight degree of solubility in water.

The development of the anti-fouling paint was based on experiments by Mallet on the effect of metallic salts upon some common marine organisms.

15.1.2 Period of Empiricism

Following this assignment for the British Association and the publication of the three reports on corrosion and corrosion protection in 1838,[16] 1840[17] and 1843[18] there followed the 'dark ages' of corrosion research.

No factual information is recorded concerning the effectiveness of this comprehensive paint system that Mallet devised. Many people about this time put forward all sorts of paint systems on the flimsiest evidence or research. Mallet however had far greater scientific understanding than most of the people devising these paint systems. He probably had more experience of investigations into this field than any other person at that time. Consequently this paint system that he devised would probably have been one of the most effective.

In 1837 Junker suggested[421] treating pipes which carried some strain, with linseed oil fused with lead oxide. This, he proposed, would fill any cavities between the pieces of iron and provide a water-resistant coating. This suggestion must have been tried and found suitable, since a report some six years later, again in Dingl. J.[422] contested this, stating that the water acquired a bad taste through this process and that in time the oil evaporated.

Zeni recommended a similar process in 1846 involving a mixture of 80parts of finely sifted brick dust to 20 parts lead oxide, all mixed with linseed oil and thinned with turpentine.[423]

15.1.3 Emphasis on surface preparation

By 1847 the importance of cleaning the material prior to applying a protective coat had become more firmly established. A solution of nitric acid, sulphuric acid and water was commonly used[424][425]. This practice appears to come from Mallet's introduction. Mallet's reports do not appear to have had a wide Continental coverage as distinct from any utterance that Faraday made. Both the 1847 papers were from British journals and there is no indication from Continental journals published about that time of any emphasis on surface preparation prior to painting.[426]

The first indication appears from a paper by Couse in 1859. He proposed the use of an alkaline solution, as distinct from an acid solution.

15.1.4 Early patents

The first patent ever taken out of a resinous nature for protection against corrosion was one by Mallet[427] in 1841. This was at the time when he would have been half way through his series of experiments on corrosion. Although the first ever patent for "colouring of shipps etc which way will prevent the eating of the worme" was taken out by Howard and Watson in 1667[428]

15.1.5 Red and white lead pigments

The first patent involving the addition of red lead, was by Cook in 1852.[429]

It was a composition of "shellac, Seedlac, gamboge(gum resin) gum arabic, gum benzoin(sumatra resin), red lead and spirits of wine; to which are added zinc oxide and french verdigis(copper acetate)"[429]

The first mention of white lead appears in a British patent published the following year in 1853 by H. Browning in which it stated:-[430]

"Grind together white and red lead without oil, black lead, with gum copal(fine transparent varnish) dissolved in spirits of turpentine"

A patent by Cram and Crane[431] in 1855 consisted of both white and red lead together with litharge, linseed oil and turpentine.

The introduction of red lead was an important landmark in the development of protective paints. It was manufactured by oxidising litharge (Pb_3O), either in furnaces or by heating the litharge with sodium nitrate. When mixed with oil no other drier were necessary, since the red lead itself is an extremely rapid drier.

White lead, which is basic lead carbonate, was produced by a process consisting of subjecting lead plates or grids to the action of dilute acetic acid and carbon dioxide. This process took about two months, although later, other processes were developed which took a shorter time. White lead was probably the most important of the white pigments.

For corrosion protective purposes red lead was found to be more suitable than white lead and for many years became the established paint to use as a base. However no proper assessment tests were to be carried out on red lead until the last decade of the century.

The next patent of significance was taken out by Redman and Martin[432] in 1863. It was a compound of "Oxidised brass or protoxide of copper, oxide of zinc, oxide of lead, and alumina." This was the first patent in which zinc oxide had appeared. Zinc oxide is a white pigment, is non-poisonous and can be used together with any other pigment. It is opaque, has good spreading properties and is a good inhibitor.

About this period the number of patents taken out began to increase. Apart from those patents which contained useful pigments, other compositions contained most unusual constituents. Bullivant[433] had one in which beef suet was included.

15.1.6. Other Pigments

A pigment which was later to prove of considerable importance was a combination of zinc and barium compounds and was introduced by J.B.Orr in 1861.[434] A solution of barium sulphide and zinc sulphate was mixed together and a compound obtained. This was to become known as lithopene and some was produced in bulk in 1868.[434]

This paint was also manufactured in Germany in 1876 when the manufacturer Bourjan produced the pigment and sold it as Orr's 'Weiss'. Orr's works were burnt down after a few years, and Orr migrated to London. Along with a partner he started the Silicate Paint Co., with a works on the Thames in 1880. He made several brands of paint apart from lithopene and exhibited at the Inventions Exhibition in 1885.[57]

15.1.7 Period of Scientific Investigation

During the last decade of the nineteenth century, the application of paint systems to prevent corrosion became more of a science than it had ever been previously.

Mallet in the period around 1840 had conducted a number of scientifically valid tests on a number of protective paint and varnish systems. For a period of some fifty years following these tests many diverse compositions were introduced, the constituents of which may each have been inert towards iron, but when indiscriminately mixed together with the aid of a vehicle sometimes produced disastrous results. No scientific method appeared to be used and few patents were worthwhile.

In the last decade, however, indications began to appear that scientific tests were again beginning to be carried out.

A mention was made by Thomson in his article on 'Notes on the oxidation and corrosion of Iron and Steel'[57] on a series of tests he carried out but unfortunately no detailed data were supplied; "....I observed that the production of a turbidity formed a very good criterion as to the protective power of certain paints and it has enabled me to make a large number of experiments with different coatings which showed

that "oxide of iron paint", white lead, and the ordinary paints of commerce had comparatively little protective influence on the iron as compared with red lead, the latter showed no signs of turbidity in the saline solution whilst all the others had become turbid and deposited a considerable precipitate of ferric oxide.

" The study of this subject was subsequently carried on in conjunction with Mr. Harry Smith which has resulted in the discovery of some valuable applications for the prevention of corrosion. I will leave him to describe these further experiments himself....."(57)

The experiments were described by Smith some five years later;(58) however this article(57) which appeared in the Journal of the Society of Chemical Industry alluded to experiments on this subject made by the Dutch Railway Company and the Cincinnati Southern Railway Company.

The Engineering and Mining Journal(435) recommended that iron surfaces should be washed and brushed with hot linseed oil, and stated that small objects should be heated until the linseed oil coating begins to fume, and that paint adheres well to iron surfaces which had been treated in this way.

In The Engineer(436) in an article on painting ironwork, the writer(anon.) insisted upon the preliminary treatment with hot oil. It also said:-

"Iron that has been vitriolled ought to be well washed and carefully dried before the paint is applied."

The Engineer of October 22nd. 1897 contained an anonymous article on 'the protection of iron by paint' The writer of this article concludes as follows:-(437)

".....The surface of the metal should be cleaned from rust and scale; the paint should not dry more quickly than is necessary having regard to the exigencies of the work in hand, and attempts should not be made, by the pressing necessity of extra driers, to hasten it.

Care should be taken that the dried film is sufficiently elastic to avoid danger of mechanical injury or of cracking when the iron expands by heat; at least three, or better still, four coats should be put on the metal in order that the covering may be as thick and non-porous as possible. Only those pigments should be employed which possess good covering power, which yield a paint adhering strongly to the metal, and which, having the lowest specific gravity consistent with these requirements and with a sufficiently low price, will carry the largest proportion of vehicle, and will accordingly allow the maximum of oil or varnish to be applied to each portion of the surface of the iron."

The Engineer of December 23rd 1898 (438) refers to tests made by Baucke with various oxides of iron pigments. In this he decided that a red oxide was the best to employ.

Probably the most comprehensive series of tests carried out were published in the last week of the century.

The author H. Smith stated:- (58)

"..During the last two years I have carried out a series of tests, which are an extension of those made by Mr. Thompson and myself in 1894 (57)

" I thought it desirable to examine and compare the paint pigments which are in everyday use as paint materials in this country, and especially to determine the effect produced by the introduction of inert pigments such as barytes (barium sulphate) and Paris white (calcium carbonate) which are employed as diluents.

" The tests were carried out in three different ways:-

1. By painting shallow iron dishes and exposing them to the action of slowly evaporating water.

2. By exposing a set of painted iron plates to the action of the weather for a period of twelve months; and

3. By exposing painted iron plates to the continuous action of water."

The results are illustrated in figs. 136 & 137

DISHES

Red-lead paint "A" red-lead paint "B" red-lead " Orange-lead " Vermilionette " Scarlet-red "	Practically unaffected.

The following are somewhat rust-stained, and are placed in order of merit:—

Zinc-white (oxide) paint "A" zinc-white " "C" zinc-white " Lithopone " White-lead " "A" white-lead " "C" white-lead "	Slightly rust-stained, placed in order of merit.

As to the 36 other paints tried in this way, all appear to have suffered equally; but it was noticed that the dish painted with boiled linseed oil simply was the first to show deterioration, and has apparently produced the greatest amount of rust.

PLATES

Paint.	Composition.	Rust from 1,500 sq. yds.
	Per Cent.	Lb.
Red lead:—		
Red lead	88·88	None
Raw linseed oil	11·12	
"A" red lead:—		
Red lead	45·00	None
Barytes	45·00	
Raw linseed oil	10·00	
"B" red lead:—		
Red lead	22·00	None
Barytes	66·00	
Raw linseed oil	12·00	
Orange lead:—		
Orange lead	88·88	None
Raw linseed oil	11·12	
**Vermilionette:*—		
Barytes	33·33	None
Vermilionette	58·80	
Raw linseed oil	7·87	
†Scarlet red:—		
Scarlet red	88·88	None
Raw linseed oil	11·12	
Pure zinc white:—		
Zinc white (zinc oxide)	87·30	Traces
Refined linseed oil	12·70	
"A" zinc white:—		
Zinc white	45·00	Traces
Barytes	45·00	
Refined linseed oil	10·00	
"C" zinc white:—		
Zinc white	27·27	Traces
Barytes	63·63	
Refined linseed oil	9·10	
White lead:—		
White lead	92·56	75
Refined linseed oil	7·44	

* "Vermilionette" is a pigment composed of orange lead on which has been precipitated about 10 per cent. of eosine.
† "Scarlet red" is red lead on which has been precipitated aniline scarlet.

Paint.	Composition.	Rust from 1,500 sq. yds.
	Per Cent.	Lb.
"A" white lead:—		
White lead	53·78	80
Barytes	40·33	
Refined linseed oil	5·89	
Pale oxide:—		
Pale oxide (about 52 % Fe_2O_3)	83·60	81
Boiled linseed oil	16·40	
Lithopone:—		
Lithopone (zinc sulphide, zinc oxide, barium sulphate)	87·50	90
Refined linseed oil	12·50	
"C" White lead:—		
White lead	50·52	95
Barytes	42·10	
Refined linseed oil	7·38	
"A" Red:—		
Barytes and calcium carbonate	78·80	118
Ferric oxide (95 % Fe_2O_3)	8·47	
Raw linseed oil	12·73	
"C" red:—		
Barytes	80·57	123
Ferric oxide (95 % Fe_2O_3)	7·55	
Raw linseed oil	11·88	
Deep oxide:—		
Ferric oxide (96 % Fe_2O_3)	86·89	123
Raw linseed oil	13·11	
Middle oxide:—		
Ferric oxide (94 % Fe_2O_3)	86·89	134
Raw linseed oil	13·11	
Extra bright oxide:—		
Ferric oxide (90 % Fe_2O_3)	82·35	137
Boiled linseed oil	17·65	
Barytes:—		
Barytes (natural barium sulphate)	88·00	135
Raw linseed oil	12·00	
Pure oxide "C":—		
Ferric oxide (90 % Fe_2O_3)	76·30	160
Boiled linseed oil	23·70	
"C" celestial blue:—		
Barytes and calcium carbonate	78·04	160
Celestial blue (a form of Prussian blue)	9·74	
Raw linseed oil	12·22	
"B" Prussian blue:—		
Prussian blue	22·76	168
Barytes	45·52	
Raw linseed oil	31·72	
Pure middle chrome yellow:—		
Middle chrome yellow	83·58	177
Raw linseed oil	16·42	
Pure raw sienna:—		
Raw sienna	74·66	197
Raw linseed oil	25·34	
Pure graphite:—		
Graphite	69·56	215
Raw linseed oil	30·44	
Pure Prussian blue:—		
Prussian blue	48·27	221
Raw linseed oil	51·73	
Pure Indian red:—		
Indian red (70 % Fe_2O_3)	82·35	227
Raw linseed oil	17·65	
"A" Vandyke brown:—		
Vandyke brown	56·70	230
Barytes	13·33	
Raw linseed oil	30·67	
"B" middle oxide:—		
Barytes	76·22	244
Oxide of iron	12·30	
Raw linseed oil	11·48	
Ivory black:—		
Drop black (charcoal black)	60·00	250
Boiled oil	40·00	
Turkey red:—		
Turkey red (95 % Fe_2O_3)	81·16	262
Raw linseed oil	18·84	
"A" celestial blue:—		
Barytes and calcium carbonate	80·56	266
Celestial blue	11·83	
Raw linseed oil	7·61	
"B" Chinese blue:—		
Chinese blue (another form of Prussian blue)	22·76	275
Barytes	45·52	
Raw linseed oil	31·72	
"A" Italian ochre paint:—		
Italian ochre	38·74	296
Barytes	19·00	
Raw linseed oil	42·26	
**"A" Middle Brunswick green:*—		
Barytes and calcium carbonate	69·99	309
Superior middle Brunswick green	18·24	
Raw linseed oil	11·77	
"C" Middle green:—		
Barytes	78·33	322
Superior Brunswick green	9·79	
Raw linseed oil	11·89	

* As mixture of lead chromate and Prussian blue.

FIG. 136 RESULTS FROM THE MOST COMPREHENSIVE SERIES OF TESTS ON PAINT PIGMENTS AND OILS CARRIED OUT IN THE NINETEENTH CENTURY (58)

Paint.	Composition.	Rust from 1,500 sq. yds.
	Per Cent.	Lb.
Superior yellow:—		
Barytes and calcium carbonate	63·07	326
Chromate of lead	22·51	
Umber	3·31	
Raw linseed oil	11·11	
English umber:—		
English umber	57·51	336
Raw linseed oil	42·49	
"A" Black:—		
Barytes and calcium carbonate	68·40	352
Carbon black	8·42	
Manganese dioxide	2·46	
Boiled linseed oil	20·13	
Burnt Turkey umber:—		
Burnt Turkey umber	59·20	353
Raw linseed oil	40·80	
"C" yellow:—		
Barytes and calcium carbonate	79·28	369
Chromate of lead	8·31	
Raw umber	1·72	
Raw linseed oil	10·69	
"C" black:—		
Barytes and calcium carbonate	79·30	392
Carbon black	4·55	
Manganese dioxide	1·20	
Raw linseed oil	15·05	
Middle purple brown:—		
Barytes and calcium carbonate	62·52	398
Oxide of iron	27·03	
Raw linseed oil	10·45	
"A" ultramarine:—		
Ultramarine	52·63	425
Barytes	26·32	
Raw linseed oil	21·05	
Burnt sienna:—		
Burnt sienna	56·00	439
Raw linseed oil	64·00	
Chinese blue:—		
Chinese blue	48·27	442
Raw linseed oil	51·73	
Boiled linseed oil:—		
Boiled linseed oil	··	500
Raw Turkey umber:—		
Raw Turkey umber	51·85	510
Raw linseed oil	48·15	

(58)

FIG. 137. A CONTINUATION OF FIG. 136

Each plate or dish was given two coats of paint, the second being applied after the first had become thoroughly dry; the tests were commenced when the second coats were dry.

Each dish was 5 inches wide by $\frac{1}{2}$ inch deep, and was filled with ordinary town water. They were not touched during a period of three months during which the tests extended although the water level was maintained.

The 49 plates were painted and exposed outside for a 12 month period.

The test results indicate quite dramatically how beneficial the red lead pigment was in preventing corrosion.

It is also interesting to note the effect produced by the inert pigments barytes and Paris white.

A pigment of high protective power, such as zinc oxide, can be seen from the experiments to be less effective by the introduction of barytes; but pigments such as chinese blue are found to be immensely improved by its presence. In his recommendations Smith says:-(58)

"I believe the best treatment for iron structures is to give them one or two coats of genuine red lead paint, freshly ground; and I would follow this up with at least two coats of either a genuine oxide of iron paint, or, in some cases of zinc-white paint made from pure zinc oxide and genuine linseed oil."

This was the state of the development at the end of the century. Some years hence the chemistry of paint systems were to be considered, but it was many years before the addition of polymers was to become a reality.

15.2 PRODUCTS DISTILLED FROM COAL AND WOOD

There is a record of tar being used as a protection against corrosion in 1826.(59)

Satisfactory results were obviously obtained since it was stated in 1836 that "the build up of rust no longer occured in pipes" which had been dipped in hot tar.(439)

Tar was also employed by Williams in 1849.[440] It appears to have been used originally just for coating and preserving timbers and with the introduction of steel plating on ships it was tried in this respect also. Since it is a thick viscous liquid it gave the visual impression of being a substance that would be a natural preservative and was consequently tried in a wide range of applications. Gradually the limitations of tar began to be realised.

The first patent[441] involving pitch or tar was taken out in 1685 by C. Correllees but this was for "preserving shipps from being eaten by worms"

A number were also taken out during the eighteenth century for this same purpose. The first taken out specifically for preventing corrosion was in 1854 by Westwood and Baillie:-[441a]

"Laying on a coating of black varnish, asphalte and naptha spirit, in order to cause asphalte and bituminous varnish to adhere better to the plates of iron ships."

In 1849 there was mention of asphalt also being used by blacksmiths to provide a brilliant black protective coating on small articles of iron.[442]

In 1878 Sucklow[442a] made the suggestion of surrounding the whole length of a cast iron pipe with a U shaped strip of pasteboard and filling the space between with asphalt as a protection against rust.

A number of patents were brought out particularly at the latter end of the century.

Askew in 1864[443] had a series of coatings. First he had a thick coating of tar over which he placed thick paper saturated in oil and applied a further coating of tar over the paper. Pinewood was then attached with iron screws and the holes filled up with wood. A further coating of tar was added.

In 1888 Nangle took out a patent for 'preserving metal'[444]. This consisted of 56 gallons of coal tar, pitch or bituminous material which was boiled for an hour with 8 gallons of cow dung straw and bark.

A number of patents were taken out about this period of this general type of composition but there is no record of them having been successful.

Patents were taken out containing an even more wide range of constituents than the last one described.

Turnbull's patent[445] for preventing corrosion of holds in ships and ballast tanks consisted of a mixture of paraffin, naphtha spirit Trinidad pitch, marine or fish glue and Portland cement.

None of these patents taken as a whole, had any scientific basis although some of the constituents had known corrosion resistant properties. The philosophy appeared to be one of 'trial and error'.

In 1895 a report[446] in Dingl J. (Anon) stated that coatings of pitch in a clinker base did not give a perfect protection in an environment in which there were changes in temperature. The sulphur content of the clinker or ashes and the porosity of the material in conjunction with any vibrations travelling through pipes, made any pipe protection ineffective.

By this philosophy of 'trial and error' the limitations of the coating were established. Within these limitations however, such application as non vibrating pipe systems are able to receive a degree of external protection.

15.3 THE USE OF CLAY, CHALK AND CEMENT

The first mention of clay and chalk being used to prevent corrosion was in 1819.[60]

Cast iron pipes were surrounded by this material in Germany. In 1826 there are records of pipes being given a limewash, allowed to lie in air and a protective thin film of calcium carbonate formed which was considered to have protective properties.[59]

Two Grenoble engineers Greymond and Vicat are reported as shielding cast iron pipes they were laying with chalk mortar in 1834. They cleaned the pipes first, then sealed one end of the pipe with

'hydraulic mortar'[447]

Payen[448] gave a report in Compt. Rend. in 1837 on the power of alkaline water to protect against rust.

The following year Mallet in his 1st. British Association Report also made a few comments:-[449]

"Lime in powder or limewash is known to have a protective power and it is in use amongst workmen.

"Cases maybe found in practice where solutions of an alkali or alkaline earth would be admissible and valuable if found effective preservers of iron; for instance, lime-water might readily replace the bilge-water in steamers, whose action is at present so destructive to the holding down bolts, boiler bottoms, coal bunkers etc. There is no reason to assume that dilute lime water would have any injurous action on the timbers of ships."

Mallet makes no further comments on this subject in either of his two later reports in 1840[17] or 1843.[18]

However a report does appear in Dingl. J. in 1843 by an anonymous contributor that:-[450]

"Tubes covered with Roman cement have problems if the flow through the pipes is great. The water in these cases taking the cement from the pipes and consequently leaving them unprotected.

The interest in these materials for protection against corrosion continued to be centred on the Continent.

In 1861[451a] there was a report of cast iron tubes covered in lime corroding.

In 1893 Wood mentioned[451] that:-

"...A mixture of good clay of at least one half of the diameter of the pipe, if allowed to dry out well before covering gives a good protection, and aids materially whatever compound is applied externally to the pipe...."

Interest in clay, chalk or cement as a preservative against corrosion in the nineteenth century, appears to have been confined mainly to the Continent for civil engineering applications in connection with pipe net works. There are few reports of any of these substances being used in Britain. A report as late as 1932 mentions in Spons Workshop Receipts that lime had only recently been introduced in an attempt to combat corrosion.

15.4 ENAMELS

Enamels may be described as a semi-opaque variety of glass applied by fusion to metallic surfaces. Although they were mentioned as early as 1463 the first detailed information about them in the nineteenth century was mentioned by Mallet in 1840. Mallet stated:(452)

"....Amongst the mechanical coverings of iron for preventing oxidation, may here be noticed the fusible enamel produced by Mariott, of London.

These are very fusible glasses, having, by the addition of large quantities of oxides, about the same expansion as the cast iron culinary vessels, to which they are chiefly applied. They are of very limited application and appear to present a good deal of technical difficulty..."

Enamelling iron with glass, was(62) first introduced into Britain from France in 1850 by Messrs. Selby and Johns, and was described as:-

"....a hard silicous glaze or covering formed upon surfaces of wrought or cast iron, so as effectually to prevent any oxidation of the metal from sea water, salts and acids..."

Timmins stated:(62)

"....Pipes for gas and water service, apart from culinary, have been enamelled upon a large scale. Upon the first introduction of this enamelled ware, the articles were sold coated grey only, and owing to their dull appearance obtained by a limited sale. In two or three years the white enamel was introduced, giving the articles a more cleaner look, which increased the demand.------Enamel has also been sucessfully applied to

corrugated iron sheets for roofing and small buildings,a purpose to which its capability of resisting the action of the atmosphere admirably adapts it."

This article was written in 1866 and from this period there is little evidence of this application for enamelling being pursued.The reason for this is probably that it was in direct competition with galvanized roofing materials which could be produced at a much lower cost and which were equally as good.

An interesting account of the state of the development of enamelling in 1880 can be found in Cooley's Cyclopedia of practical receipts.

It is described as :-(453)

".....a species of vitreous varnish coloured with metallic oxides,applied in a thin stratum to brightly polished metallic surfaces on which it is fused by the flame of a lamp urged by the blowpipe or by the heat of a small furnace.The basis of all enamells is a highly transparent and fusible glass,called 'frit''flux' or 'paste',which readily receives a colour on the addition of metallic oxides."

One of the preparations mentions a mixture of 16 parts red lead;3 parts of calcined borax,12 parts of powdered flint glass fused together for 12 hours,then poured out into water and reduced to a powder in a biscuitware mortar.

A variety of colours was able to be obtained by varying the constituents.Enamel black,blue,green,white,orange,purple,and violet are amongst those mentioned.

Although many formulae were tried at this time,a degree of appreciation was known regarding the effect that various factors had upon the final product.The report stated;-(453)

"The precise qualities of the products of the processes depend greatly upon the duration and degree of heat employed.By increasing the quantity of sand,glass or flux,the enamel is rendered more fusible,and

and the opacity and whiteness is increased by the oxide of tin. The use of borax should be avoided, or it should be used sparingly, as it is apt to make the enamel effervesce and lose colour."

An interesting account of the actual process towards the end of the century was described by Wagner[454] in his book on Chemical Technology.

"The surface of the cast iron to be enamelled is first carefully cleaned by scouring with sand and dilute sulphuric acid, next a thickish magma, made of pulverised quartz, borax, feldspar, kaolin and water is brushed over the clean metallic surface as evenly as possible, and immediately after a finely powdered mixture of feldspar, soda, borax, and oxide of tin is dusted over, after which the enamel is burnt in by the heat of a muffle."

Wrought iron was found to be more easily enamelled than mild steel. One of the troubles appeared to be the presence of black spots on the surface of the enamel due to an imperfect fusion with the base material. The cause of these imperfections appeared to be connected with dirt on the surface or with the composition of the materials.

The enamels gained a high favour in Britain, mainly with culinary uses and in this connection had no competition from galvanizing. Galvanized materials had been tried in this connection over a century before, in France, but were discarded because of the poisonous nature of the juices produced by the action of the liquid on the galvanized material.

CHAPTER 16

COMPARISON OF THE INDUSTRIAL AND SOCIAL CONDITIONS OF THE WORKERS

16.1 CONDITIONS OF EMPLOYMENT

Contrasting the conditions under which men, women and children worked, there was a considerable distinction between the hot dipping and the electro plating types of processes.

Smee,[328] who was a surgeon, summarised the position well when he stated:-

"-----I believe the mode of working in metals by the galvanic fluid is more wholesome, and attended with far less deleterious properties, than the methods now practiced------"

The two processes associated with hot dipping i.e. galvanizing and tin-plating shared many of the same problems. Galvanizing, then as now, was not a pleasant occupation.

The main discomfort that galvanizers had to suffer was from inhaling unpleasant gases and vapours generated during the process. There was also a secondary danger from burns and bronchial infections which were necessarily incidental to any occupation conducted in open sheds, where alternate exposure to great heat and cold draughts cannot be avoided.

Galvanizing was carried out in the wire industry and in 1871 a mortality table[316] was published for that year (fig.138). The table indicates the wide age range of the people employed at the time.

AGE RANGE	UP TO 5	5-10	10-15	15-20	20-25	25-35	35-45	45-55	55-65	65-75
DEATHS	1	1	2	14	17	15	16	18	16	7

FIG.138 [316]

The voices of protest began to grow about the conditions of employment and many works installed cowls or hoods, some of which were connected to mechanical fans and installed over the pickling vats and galvanizing baths.

A government committee was set up in 1899[81] to investigate all types of dangerous trades in the country and on visiting many galvanizing works they found that a number of the fans installed were not in proper working order due to the corroding action of the fumes. When the fans failed, ventilation ceased since the natural openings in or near the roof had been closed to assist the suction power of the fan, so that the movement of air immediately above the bath or vat was obstructed by the cowl. Following these investigations a more regular inspection of fan installations was carried out.

During break times it had been the custom for the galvanizers to eat their meals squatting down by the side of the vats. Following this government investigation, employers were encouraged to provide a room in which the workers could sit down to have their meals away from the unpleasant taste and smell of the fumes.

Galvanizing is very unclean work, but it is noted that no recommendations were made in this report for the provision of wash houses for the workers. At this time however, such proposals would have probably been considered revolutionary, since similar facilities were not in existance in other industries and in fact were only finally implemented into the galvanizing plants as late as the mid-twentieth century, fifty years later. This was the only investigation that the government made into the conditions of employment of galvanizers in the nineteenth century.

Other problems common both to galvanizing and tin-plating were those of burns due to the splashing of liquid metal and fumes from the pickling tanks.

Fortunately in tin-plating, fumes from the liquid metals were not as distasteful as those from molten zinc, but a problem arose from grease pots when animal fats were used. This caused some operators to be sick, but the effect was considerably reduced when palm oil was used. Reports on the conditions of employment within the electro plating industry were considerably better.

Aitken gives a very favourable impression of working conditions:-

" The workmen and women employed in electro plate manufacture occupy a high position among artisans. The business is a clean and healthy one. On examination it will be observed that one sixth of the labour is performed by females." (SEE Ref. 455)

An interesting comment was given by Ryland[455a] on the influence of the trade upon workmen.

" The occupation is pleasant, the labour light, clean and remunerative and the impression produced on the mind and heart by the study of fine forms of decoration carried out is the highest character of workmanship....."

One of the few problems appeared to be that of finger discolouration due to contact with the metallic solution and the possibility of some of this consequently coming into contact with food. Care had to be taken in operating cyanide baths but skilled operators were employed for this. Dangers are present in most industrial processes however, if proper care is not taken.

In the process of sherardizing, conditions were not good. Steam and acid fumes were present from the large pickling tanks and zinc dust in the air must have made the working conditions difficult. It is recorded[98] that zinc dust was dumped on the floor and tramped under foot. On several occasions the works became flooded by water. However by the end of the nineteenth century when this process was developed, workers had far greater protection

in law, and consequently the large pickling tanks were removed from the building and reconstructed outside for the benefit of all concerned.

Little is recorded about the social character and living conditions of galvanizers, tinplate workers and electroplaters. However a Birmingham witness, in the Children's Employment Commission for 1865 stated that :-

" Wire workers are generally of the roughest and most ignorant class, probably next to nail workers. The language of some of them is disgraceful. "

It is possible that galvanizers would very well have fitted into this category. They probably lived very close to their employment in the hovels that existed at that time. Skilled electroplaters could well have been able to have owned their own property. It is possible however that in many cases their social life would not have been different from that of the other workers.

Tinplate workers, as distinct from galvanizers and electroplaters would probably have lived more within an agricultural community.

16.2 CHILD LABOUR

From the early part of the nineteenth century there had been considerable concern from many quarters about the conditions of employment in factories, especially the working conditions of children.

Throughout industry young children were paid very low wages for doing work which otherwise would have to have been done by women or men. Consequently during the nineteenth century in particular, there was this continual conflict of interest between the employers on the one hand, and those interested in childrens' welfare on the other. There were of course, many employers who took a genuine interest in the welfare of the employees and children in particular, but in general they were loathe to concede any benefit which meant a reduction in profit.

There was also a general ignorance about the conditions of employment in factories amongst many of the Members of Parliament, although a number of them were factory owners.

As a consequence of this a Commission on the Employment of Children in Factories was set up in 1833 and a further Commission on the Employment of Children in 1841.(456)

From the reports of these commissions as they apply to employment in tin-plate works, it would appear that in the manufacture of the plate a large proportion of workers were boys who were principally employed on ancillary work, such as opening and separating the iron-plates after being cut to final size, attending furnace doors, and drawing the plates through molten grease and tin metal.

The girls employed appeared to be in the older age group of 13 to 18 years of age. They worked from eight in the morning to six in the evening and had a half hour break for breakfast and an hour for dinner.

Children were also often exposed to a high degree of heat, but this would probably have been for only limited periods in many cases. Many of the children were wheeling slag and other ash and consequently when they left the actual furnace area to tip outside, this heat effect would diminish. However in R.W. Jones' report to the commission, he stated:-(457)

".....the surgeon of the works expressed an opinion, grounded on his experience, that their constant daily employment in the rather heated temperature of the tin works produced in them a constitutional derangement, which, if it did not absolutely prevent them following their occupation, kept them frequently under his care. The usual temperature of the tin works is stated to be 60 degrees, and the highest temperature in which young persons are employed is from 70 to 80 degrees. "

In another part of the report(456) the buildings are described as being 'well ventilated or open'

It can be appreciated that children and also other operatives would be prone to influenza in winter time, continually moving between the extremes of temperature.

Accidents in the iron and tin works consisted of;-(458)(459)

'burns and slight contusions'

Regarding childrens' moral and educational welfare, managers and owners were continually on the defensive, stressing wherever possible such features as "regular attendance at Sunday School", indicating that the childs' moral welfare and education was not being ignored. With the job description of a Mr. Charles Hathaway it states that he "also superintends the Church of England Sunday School." This was obviously trying to impress on the Commissioners what fine upright men were in charge of the children. A reference to Sunday school or public worship is made on twelve occasions within six pages of the report. Interesting parts of the report are given in figs. 140 to 145.

Stanford gives details about child labour in the tinplating works:-(289)

"Youths of all ages are employed under the tinplate workers, and pressing blank trays etc. Four or five boys are employed by each tinner in the larger works. In the painting shops young persons, male and female are employed with adults."

FOREST OF DEAN.

Report by *E. Waring*, Esq.

than to others (*vide* Nos. 3, 4, 5, and 7), and is certainly very likely to offend the nerves of delicate or dyspeptic stomachs.

94. This effect is most probable where animal fat is employed: but palm-oil has long been extensively used in this process, and its fumes are far less unpleasant. There is, however, some objection to it, on the score of economy, in consequence of its evaporating more freely than animal oil; and a combination of the two is now most commonly adopted.

95. The work of the females does not appear capable of doing them any harm, provided they observe common cleanliness, in washing off the dust that clings to their pores, when they leave work.

96. Their appearance indicated the common average of health. Some of them are handsome and well-formed girls, and when dressed to advantage in their holiday trim, bear comparison with the most blooming of the peasantry.

97. Accidents in the iron and tin works, consist principally of burns and slight contusions. The shears, which are worked by powerful machinery, sometimes curtail the fingers of careless operators, who look another way whilst laying the plates under their edges. The loss of one or two finger tips, generally operates as a sufficient warning for the future.

98. I did not remark any gross inattention to fencing off the more dangerous parts of the machinery; but there is more precaution in this respect, at some works than at others.

FIG.140 REPORT OF THE ROYAL COMMISSION ON EMPLOYMENT OF CHILDREN 1842, 17,8 ,

FOREST OF DEAN.

Lydney Tin Works.

Forest of Dean.

Evidence collected by *E. Waring*, Esq.

March 16, 1841.

No. 1.

No. 1. *John James*, Esq., carrying on Tin-plate Works and Rolling-mill at Lydney, under the firm of John James and Son.

We employ about a dozen children under 13 years of age; the youngest eight or nine years old; say a dozen lads, and as many girls, above 13, and under 18 years of age. The hours of work are from eight in the morning to six in the evening for the girls, some preparation being necessary before they can begin their labours. The men and boys work from six to six; there is no night-work; they are allowed half an hour for breakfast and an hour for dinner. They usually take those meals in the works, except a few who live close by. The boys open iron-plates after shearing, *draw* and *list* tin-plates, attend furnance-doors, and act as sledge-boys in the smith's forge. The girls scour and rub the tin-plates. I do not consider any part of the process injurious to health. One boy was killed, about seven years ago, by incautiously and needlessly coming into contact with a rolling-mill. Fingers, or fingers' ends, are occasionally amputated by the shears whilst the boys are heedlessly looking away from the work. No boy under 13 is allowed to oil the gudgeons, or attend to any machinery while in motion. We never have had an accident from the practice. All our work is job or piece-work. Some of the youngest boys do not earn more than from 2*s.* to 5*s.* a-week. They earn money in proportion to their skill and quickness. Boys over 13 earn from 5*s.* to 10*s.* a-week. The girls earn from 5*s.* to 7*s.* a-week. We have no girls under 13 in our employ. The wages are always fixed by ourselves, but they are paid by the men who employ the children under them. We admit of no corporal punishment. It is a rule with us never to receive back any individual who has been discharged for bad conduct. I consider the general health of the children quite equal to that of the population at large.

There is a national-school at Lydney under the patronage of Mrs. Bathurst, of Lydney-park. There is also a Sunday-school held in the town-hall, at which my son always attends, and one of our clerks is the master, regularly conducting the children to church. There are numerous *dame-schools*, and two adult schools, in Lydney, at low charges; perhaps 6*d.* per week. I should think not more than a moiety of the children, and juniors in our employ, attend the Sunday-school.

Mem.—Only two processes in the tin-plate manufactory appear to me at all likely to affect the health. One is the *pickling* of the iron-plates in a strong infusion of sulphuric acid, the fumes of which sometimes affect the eyes and the stomachs of men employed in that branch; boys are never so employed. The other is dipping and drawing the plates through boiling grease, preparatory to tinning. At this the boys frequently work, and the fumes are certainly offensive, particularly where animal fat is employed. When palm-oil is used, unmixed with tallow, the smell is not unpleasant; but the greater volatility of this oil, when heated, is said to render it less economical than tallow, or an admixture of the two. In either case the free circulation of air, through the open sheds in which the work is carried on, must materially correct any injurious tendency of these evaporations. I have not discovered that any but boys of delicate constitutions, suffer more than a temporary inconvenience from them.

No. 2. Mr. *Charles Hathaway*, aged 35, Manager of Messrs. James's Tin Works at Lydney; also superintends the Church of England Sunday-school.

No. 2.

I have been in the works from my boyhood. I do not observe any permanent ill effect on the health of the boys and girls employed in our works. For a few days, when they first come, they appear to suffer a little from the dust and heat, but it soon goes off by habit. Whenever the children use profane language, I reprove them severely for it, and reason with them on its sinfulness. The girls use quite as much bad language as the boys; the girls are too frequently unchaste in their conduct. Illegitimate children are not frequent; one young woman has lately been dismissed on that account. I am sorry to say there is too general a propensity to stealing coal and wood from the works.

The children do not manifest a disposition to avail themselves of the Sunday-school to the extent I could wish. Their parents often send them, but they play truant on the road. Books are given to the more diligent scholars, as rewards of merit.

In most cases they are cleanly in their habits; some are contented with being always dirty. We have one whole family belonging to the latter class. There are two sets of privies in the works, originally appropriated to the separate sexes, but it is difficult to make them mind this distinction. I never heard of the boys and girls using them at the same time.

No. 3. *Samuel Pritchard*, aged 14 next April. No. 3.

Has worked four years in the Lydney Tin Works. Says the smoke from the grease-pots makes him feel sick; cannot eat his dinner one day in two; has not mentioned this to the manager; was quite healthy before he came into the tin-works; went there at his father's desire; his father is a labourer in the works, earning 12*s.* a-week. When at full work earns 6*s.* 10*d.* a-week; has 2½*d.* for every three boxes; draws the plates out of the grease; reads and writes; goes to the Sunday-school and to church; is never struck by the overlookers; Mr. Hathaway, and all, treat them very well always.

Mem.—This boy appears to have delicate stamina, but is well grown.

No. 4. *Edward Jones*, aged 12 last February. No. 4.

Has worked one year at the Lydney Tin Works; likes his work very well; is a *lister*, *i. e.* melts off the ridge of molten tin collected in the lower edge of the tin-plate after dipping. Earns 5*s.* 6*d.* a-week; can read and write; went to a boarding-school at Aylburton; his father is a *sorter* in the works, and earns from 30*s.* to 40*s.* a-week. Has a class of little boys at Mr. Nicholson's Sunday-school,* and goes to the Baptist chapel. Is very healthy, and does not find the smell of the hot grease disagree with him; thinks the boys in the works who do not attend the school are not so diligent as those who do.

Mem.—This is a superior kind of boy, in manners and person, and appears remarkably healthy.

No. 5. *Samuel Whittington*, aged 14 next May. No. 5.

Has worked in the Lydney Tin Works about three years; draws the plates out of the grease; likes his work; does not find the smell of the hot grease make him sick; earns 6*s.* 10½*d.* a-week; his father is a roller in the works; reads a little; goes to the Sunday-school and to church.

Mem.—This is a very robust, ruddy-visaged boy.

No. 6. *John Jenkins*, aged 16 last November. No. 6.

Sorts the plates before they are pickled; has been at this work three or four months; worked with his father in the *scaling*-room for four or five years; earns 5*s.* a-week; earned the same in the scaling-room; is paid by the week; the boys who work by the piece earn most money. I take my wages to my mother; father's dead; one brother earns the same; there are five little sisters at home; can read and write; goes to Mr. Nicholson's Sunday-school and to chapel regularly; thinks the boys and girls who have not learnt to read, and do not go to the Sunday-school, are more idle and "more wickeder" than the rest.

No. 7. *John Turner*, aged 15 last October. No. 7.

Is a *lister* in the Lydney Tin Works, and earns 5*s.* 6*d.* a-week; would rather work out in the yard, because it agrees with him better; does not like the smell of the hot grease; cannot eat his dinner very well after it; has worked at *listing* two months; was four years in the scaling-room; some of the boys never get used to the smell; always ate his victuals very well before he worked in it; goes between four and five in the morning to get the pots ready, *i. e.* to light the fires and put in the grease; begins work at eight, and leaves off at six; has an hour for dinner; reads a little; attends Mr. Nicholson's Sunday-school and chapel.

Mem.—This boy's appearance is delicate.

FIG. 142 REPORT OF THE ROYAL COMMISSION ON EMPLOYMENT OF CHILDREN, 1842, 17, 15.

REPORT by RHYS WILLIAM JONES, ESQ., on the Employment of Children and Young Persons in the Cwmavon Iron-Works, Collieries, Tin-Works, and Copper-Works, and in the Oakwood Collieries, near Port Talbot, Glamorganshire; and on the State, Condition, and Treatment of such Children and Young Persons.

CWMAVON IRON-WORKS, &c.

Report by *R. W. Jones*, Esq.

TO HER MAJESTY'S COMMISSIONERS.

GENTLEMEN, *August* 24, 1841.

1. THESE works are situated near Port Talbot, in Glamorganshire, and are now carried on by "The Governor and Company of English Miners," and embracing, as they do, so many departments, they are, collectively, the largest manufacturing concern in that part of the county.

2. I have had several opportunities of inspecting these works, and the printed returns from them have been fully filled up.

3. The agents of the iron-works and mines state that they employ in that department 438 persons, out of which 50 are between the ages of 13 and 18 years, and 20 between the ages of 9 and 13 years, all males, and that there is not one female employed in the iron-works and mines.

4. The youngest boys are employed to attend to the air-doors; those about 15 years old drive the horses and fill the trams, and those above that age generally assist the miners in digging and getting the coal and ironstone.

5. They work eight hours in the day, and very seldom have night-work. The majority of the children and young persons are employed by the company, or masters, at day or weekly wages, varying from 4*s*. to 18*s*. per week, according to age of the boys and the nature of the work performed.

6. They are nearly all reported regularly to attend public worship, and out of the 70 employed 49 are said to be able to read, and 19 have signed their names to the return; four only are reported to have lost time from sickness, three from accidents in the works, and one from cold.

7. The two iron-furnaces at these works are not suspended on the Sunday. The agent states that "when repairing the machinery they find their furnaces cool, scour, and make bad iron, if stopped for many hours."

8. Every other part of the works is suspended on Sundays.

9. The agents for the forges and tin-plate manufactory state that they employ in these departments 200 persons, (166 males and 34 females,) out of which 29 males and 14 females are between the ages of 13 and 18 years, and 21 males and 3 females between the ages of 8 and 13 years. The youngest boys are employed about the tin-works in dipping the plates into grease at the annealing house, and in bundling the shearings of the black plate together for the forge; the others are employed in the various works of the tin-works and forge, and some few of the eldest work at night every alternate week.

10. Their wages, varying from 2*s*. to 10*s*. per week, are mostly paid by the master, and average about 6*s*. per week each; but their principal work is by the piece, and their period of labour is about 10 hours per day.

11. The youngest girls are about 12 years old; only three of them are under 13 years old, and they are all employed in the tin-works in scouring, rubbing, and opening the plates; they work from 8 to 10 hours per day, but never at night.

12. They are paid by the master from 3*s*. to 6*s*. per week each, according to the nature of the work they perform, which is mostly by the piece.

13. The boys and girls are nearly all reported to regularly attend public worship, and of the boys, 49 are said to be able to read and 16 have signed their names to the return; and of the girls, 19 are said to be able to read, and four have signed their names to the return.

14. Their health is said to be very good, and very few of either the boys or girls have been known to lose time from sickness.

15. Most of the young females gave the same account of their good health; but the surgeon of the works expressed an opinion, grounded on his experience,

FIG. 143 REPORT OF THE ROYAL COMMISSION ON THE EMPLOYMENT OF CHILDREN, 1842, 17.

that their constant daily employment in the rather heated temperature of the tin-works produced in them a constitutional derangement, which, if it did not absolutely prevent them following their occupation, kept them very frequently under his care.

16. The usual temperature of the tin-works is stated to be 60 degrees, and the highest temperature in which children or young persons are employed from 70 to 80 degrees.

17. The agent of this department states, in answer to the printed queries, that a limitation of the age at which children are employed to 10 or 11 years would be desirable, because close application to work at an earlier age injures their health and stints their growth.

18. Night-work is only necessary in one part of the works—that part is the mill, which is kept in operation day and night, so as to keep the other parts of the manufactory properly at work during the day, which otherwise could not be done, and the consequence would be a serious loss to both master and men. The mill-men change their day and night turns every alternate week, each turn lasting 12 hours.

19. No night set of children are employed, but young persons are employed at night at the mills; and any prohibition in respect to them would most seriously affect them in the mill departments, where night labour is indispensably necessary.

20. The time allowed for meals is half an hour for breakfast and one hour for dinner, in summer, and half an hour in winter; and at night one hour and a half is allowed for rest and meals at different times.

21. They have no system of rewards, but the punishment for neglect and inattention to their duty is by way of paying a small fine, which is appropriated to their education: no corporal punishments are allowed to be inflicted.

22. There is a very marked difference in the skill and general character of the hands who have been employed in the works from infancy and those who have been taken into such employment at later periods.

23. There is here a school, which is supported by monthly contributions of 3*d.* from each of the workmen, and also by fines inflicted for dereliction of duty and impropriety of conduct.

24. This school is exclusively for the workmen's children. There is likewise a sick-fund, supported also by monthly contributions of 10*d.* per man and 4*d.* per boy, whose weekly earnings are under 10*s.*, the funds of which are appropriated to the relief of such men and boys as are unable to follow their daily occupation through illness or accident.

25. The amount of relief given on these occasions is 5*s.* per week to each man and 2*s.* 6*d.* to each boy during the continuance of their sickness or inability to work. This relief is paid on the production of a certificate signed by the surgeon of the works and the agent by whom they were employed: there is also an annuity allowed to the widows of such men who had been employed at the works for a period of six years, the amount of which annuity is regulated according to their necessities.

26. At the copper-works they employ 10 men and boys and 3 girls, who are about 14 years of age, and who wheel out the ashes; they work from six to nine o'clock in the morning and from four to six o'clock in the evening, and get 1*s.* per day; 13 of the boys are between 13 and 18 years old, and 12 between 9 and 13 years old.

27. The youngest boys are employed in wheeling out ashes, and earn from 2*s.* 6*d.* to 4*s.* per week; the oldest boys wheel out slag and attend the masons, and earn from 5*s.* to 10*s.* per week.

28. They are reported to regularly attend the Sunday-school and public worship;

employ 20 children and young persons, 10 of whom are between the ages of 13 and 18 years, and 10 between the ages of 10 and 13 years.

34. The youngest, and indeed the most, of the boys are employed to cart or draw the coals from the stalls to the mainways, in the levels, and to attend the air-doors; but some of the eldest are employed in driving the horses and working with the blacksmiths; they work about nine hours per day, and have no nightwork.

35. Their wages are from 8*d.* to 2*s.* per day, according to the work they perform, and they are all but three employed by the men, who do the work by the piece.

36. Thirteen of them are reported to attend the Sunday-school, all regularly attend public worship, five can read, and one only has signed his name to the return.

37. There do not appear to be any young females employed at these collieries.

38. With regard to the schools at Cwmavon, Mr. Benjamin Rosser, the schoolmaster, states:—

I am a teacher in Cwmavon Sunday-school; the hours for which it is open are from nine until half-past ten o'clock, and the children are conducted thence to the parish church.

I have a day-school, which is open from nine o'clock in the morning until twelve at noon, and from two to five o'clock in the afternoon; and from seven to nine o'clock in the evening for the working population.

In the school above mentioned there is also a female teacher; the children are taught to read and write and cipher, and likewise needlework; the hours at which it is open are from nine o'clock in the morning until twelve at noon, and from two to five o'clock in the afternoon. I have 80 boys attending the day-school, and the mistress has from 60 to 70 girls; we have about the same number attending the Sunday-school. The evening-school is not so regularly attended throughout the year; in winter I have from 30 to 40 children and young persons attending, and in summer from 16 to 20 on an average. All are the children of miners, colliers, or persons engaged in the iron, tin, and copper trade.

The children are taught to read, write, and cipher, in the English language.

Children are removed from the school from 9 to 10 years old; very few are left in school until 12 and 13 years of age.

To a certain extent I think the removal so early from school does operate to the injury of the children in after-life; for they come in contact with persons of depraved habits at a period when their minds are most susceptible of any impression; good impressions being neglected, their minds oft become the recipients of those which are bad.

I think they ought to be allowed to remain in school, certainly, from 13 to 14 years of age.

I think Sunday-schools are calculated to teach children their moral and religious duties, but certainly are not sufficient to make up for the loss of instruction and early removal from the day-schools; nor are they calculated to bring them on in mathematical instructions, so as to qualify them for situations in after-life requiring that knowledge.

I think, certainly, the progress of those unemployed is far superior to those partly engaged in labour; because when they are put to school at an early period, and their minds well cultivated up to 14 years of age, whatever education they may receive then will be well-grounded. On the whole, I should say, the education of children is grossly neglected and ought to be looked into.

I have the honour to be, Gentlemen,

Your obedient servant,

R. W. JONES.

CHAPTER 17

CONCLUSION

At this stage the place of corrosion technology in the nineteenth century can be viewed in perspective within a number of contexts.

If we draw together the cords of the various parts of this subject, we can see that nearly every aspect of scientific and technological development within this period is in varying degrees interlocked with every other, through the problems that corrosion has caused.

Corrosion technology can consequently be seen to be one of the common factors embracing the many sided aspects of the industrial revolution.

We have seen through this work that although corrosion has been a common problem in the various types of industrial developments, the study of the subject, apart from some notable exceptions, was not given the importance that was justified. This was primarily because corrosion in most cases tends to be a long term effect and consequently it tended to be low on the list of priorities in investigations. Any investigations that did take place were carried out in cases where the result of corrosion was either dramatic, through rapid failure, or when the cost factor was appreciated. When experiments were carried out, corrosion investigations usually formed a small part of a much wider programme and little data was usually published.

Although corrosion technology embraced most aspects of the industrial developments in the nineteenth century, there was little interaction between the constituent processes. There could have been a wider sharing of knowledge for mutual gain, particularly between the tinplate and galvanizing industries. Apart from a lack of useful published information, there were also sociological and geographical restraints.

Government involvement in various associated aspects was varied. A number of corrosion investigations were carried out under the auspices

of the Admiralty. Legislation was mainly within the framework of conditions of employment and safety. The coverage of this legislation was wide, ranging from boiler management to galvanizing and tin-plate manufacture.

The degree of participation by scientists and technologists working in these fields has varied considerably. Scientists tended to play a major part during the initial period when a particular principle or process was becoming established. Their interests would then transfer to other problems. The interest of technologists tended to be generated if there was the prospect of financial gain. They would take over particular processes where the scientists had left them, for commercial development.

As distinct from many of the technologists, a considerable number of the scientists were well educated in other fields, such as Cresson, Smee and Wright who were medical doctors and had 'science' more as a hobby. Since many of them had a high educational attainment and a genuine interest in promoting scientific knowledge, there was a greater tendency for their investigations to become more widely known through journals and meetings. With technologists tending to have a greater interest in financial motives, many of them were cautious and unwilling to allow information to become freely available. In general, scientists had a greater involvement with non-ferrous metals whereas technologists were interested in the construction metals, iron and steel.

During the present century there has been a great growth in the variety of metals and situations investigated.

As the applications for non-ferrous metals increased and the environments in which they were situated became more varied, then it became increasingly necessary for the scope of corrosion investigations to multiply. Sustained attempts have been made to try and understand the nature of particular types of corrosion, sometimes only to the extent of establishing reliable test methods, but often to develop in some depths the scientific understanding of the processes themselves. (460) (264a)

Attempts have been made to establish the conditions that lead

to serious corrosion of metals in the atmosphere[462][463] particularly the influence of relative humidity, of polluting gases[464] and contaminating particles. This has helped to prevent corrosion during manufacture, packaging, storage and transport of metal articles throughout industry.

There have been detailed investigations over many years on the effect of water flow, aeration, pressure and temperature in determining corrosion rates, together with the effect of corrosion salts and corrosion inhibitors.[465]

The physical structure and the chemical composition of films of oxide and of corrosion products have been studied in great detail in connection with the mechanisms of oxidation, corrosion and inhibition. Methods involved have included film-stripping, x-ray and electron diffraction, electron microscopy and the use of radioactive isotopes.[466]

Dry oxidation and tarnishing of metals at high temperatures have been investigated. It has been shown how the nature and rate of oxidation can vary with time and how the changes with passage of time depend both on the nature of the metal and the conditions of exposure, such as temperature and purity of the atmosphere.

The principal features of the mechanism of bacterial corrosion, especially that causing serious trouble in waterlogged clay soils, have been established. This has been possible only by the combined use of electrochemical, microbiological and biochemical methods specially designed for the purpose.[467]

With an increasing understanding of corrosion processes it has been possible to apply this knowledge in determining methods of controlling and preventing corrosion in many types of industrial situations.[468]

A process for the anodic oxidation (anodizing) of aluminium in a chromic acid bath has been devised and it has proved to be a very effective process for producing corrosion-resistant oxide films on aluminium. It has also been discovered that the films could be coloured

by suitable dyes.(469)

Sodium benzoate is used as a valuable corrosion inhibitor for steel. Paper impregnated with sodium benzoate is widely used in packaging bright steel products such as razor blades and needles, and it is used also in various temporary protectives. A mixture of sodium benzoate and sodium nitrite (1.5.% sodium benzoate and 0.1 % sodium nitrite) has been found to be very effective as an additive either to water or to glycol antifreeze for preventing corrosion in cooling systems of motor vehicles.(470)

Methods for determining the aggressiveness of soils in which it is intended to bury pipework have been worked out, so that contractors can decide on the optimum degree of protection required at various points along any given pipeline route.

The conditions in which a variety of corrosion-inhibiting substances are most effective have also been established, especially the minimum safe concentration of inhibitors required to counteract particular concentrations of corrosive salts, such as chlorides and sulphates, in water.

Other protective methods that have been investigated and are a continuation of work done in the nineteenth century are the inclusion of small amounts of copper, chromium, nickel and molybdenum in steel, the development of natural and artificial patinas on copper, the use of phosphate coatings on steel and the formulation of corrosion inhibitive paints.(471)

During the nineteenth century the metals used in constructional work were iron and then steel. During the twentieth century aluminium alloys are replacing iron and steel in many of their traditional roles but the problems of stress-corrosion cracking of the welded material present many problems.

The first weldable Al-Zn-Mg alloys were developed in Europe in the 1940's but little U.K. interest appeared evident until 1958 when

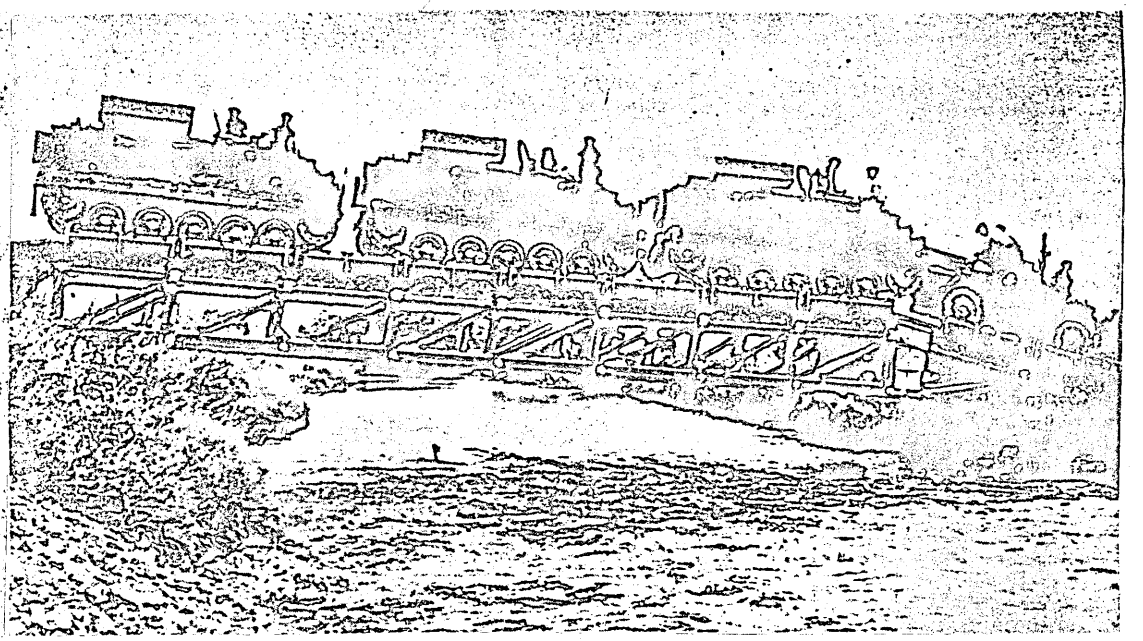


Fig.146 ALUMINIUM ALLOYS HAVE REPLACED THE TRADITIONAL NINETEENTH CENTURY CONSTRUCTIONAL METALS IRON AND STEEL IN MANY APPLICATIONS.THIS IS A TRANSPORTABLE BRIDGE USED FOR MILITARY TRANSPORT BY N.A.T.O. THEY ORIGINALLY FAILED THROUGH STRESS-CORROSION CRACKING AT THE WELDED JOINTS.

M.E.X.E (Military Experimental Establishment) became interested in their application to military bridges.At the time,the strongest and lightest bridges used by the Army were fabricated from high strength non-weldable Al. alloys by rivetting.The weldable Al-Zn-Mg alloys,although slightly weaker in the unwelded condition,appeared capable of offering considerable weight savings because of the greater flexibility of designs rendered possible by a change of welded construction.

Throughout the early 1960's M.E.X.E designed and developed to prototype stage a new military bridge known as the medium girder bridge, from Al- 4% Zn- 2% Mg material(fig 146).There were, however,problems with stress-corrosion cracking around the welded joints.It was found that using this alloy in the air-cooled duplex aged state, no further failures were recorded.(472)(473)

In 1966 a short power line to carry d.c. electricity was built in Sweden and the towers consisted of tubes with flattened ends bolted to the vee-shaped vertical extrusions.Soon after erection,cracks were observed at the flattened tube ends,which were found to have been caused by stress-corrosion.However with a solution treatment followed by water quenching before the flattening,the problem was solved.(474)

Davy in the nineteenth century suggested that bolts fastening sheathing to ships should be made of an alloy only slightly more noble than copper. A procedure to some degree analogous to this is practiced at the present time to prevent the corrosion of iron bolts used in the mechanical joints in certain present day pipeline systems.By making the bolts of an alloy steel slightly cathodic to iron and steel,it is expected that the bolts will be cathodically protected by corrosion of the surrounding metal.

The electrolytic theory of corrosion and some of the present day problems of galvanic corrosion and corrosion protettion were to an extent anticipated by Davy,without the benefit of electrical theory or even electrical measuring and recording devices.His explanation for the corrosion of copper in sea water as being due to an electrical effect

associated with local deposits of oxides and chlorides of copper does not differ materially from the modern explanation of the same phenomenon.

The toxicity of copper salts towards marine organisms is currently receiving active consideration in the selection of copper alloys for marine use. With respect to cathodic protection, Davy realised the necessity for control of the current required for corrosion prevention, as do modern corrosion engineers. Just as Davy failed to control the cathodically applied current so as to prevent both corrosion and fouling, so there remains today the problem of accurately measuring the minimum current required for corrosion prevention and establishing suitable criteria for cathodic protection under all conditions.

Although a far greater intensity is now applied to the study of corrosion, the cost to society continues to spiral, the most recent estimate mentioned in 1974 by Duke being £1,365,000,000[475]

Many of these structures were built during the late nineteenth century during a period when the important investigations of Mallet should have been expanded.

Consequently we are reaping the problems brought about by this lack of foresight.

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